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Wisconsin Power Plant Impact Study

by

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OFFICE OF RESEARCH AND DEVELOPMENT
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FOREWORD

The U.S. Environmental Protection Agency (EPA) was created because of increasing public and governmental concern about the dangers of pollution to the health and welfare of the American people. Polluted air, water, and land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated attack on the problem. Research and development, the necessary first steps, involve definition of the problem, measurements of its impact, and the search for solutions. The EPA, in addition to its own laboratory and field studies, supports environmental research projects at other institutions. These projects are designed to assess and predict the effects of pollutants on ecosystems. One such project, which the EPA is supporting through its Environmental Research Laboratory in Duluth, Minnesota, is the study "The Impacts of Coal-Fired Power Plants on the Environment." This interdisciplinary study, involving investigators and experiments from many academic departments at the University of Wisconsin, is being carried out by the Environmental Monitoring and Data Acquisition Group of the Institute for Environmental Studies at the University of Wisconsin-Madison. Several utilities and state agencies are cooperating in the study: Wisconsin Power and Light Company, Madison Gas and Electric Company, Wisconsin Public Service Corporation, Wisconsin Public Service Commission, and Wisconsin Department of Natural Resources. During the next year reports from this study will be published as a series within the EPA Ecological Research Series. These reports will include topics related to chemical constituents, chemical transport mechanisms, biological effects, social and economic effects, and integration and synthesis.

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ABSTRACT

Water quality parameters of a 192-ha (480-acre) cooling pond adjacent to the Columbia Generating Station, Portage, Wisconsin, has been investigated. Analyses were made for major and minor elements, nutrients, pH, alkalinity, O_2, chloroogranics, phenols, and polyaromatic hydrocarbons. Similar parameters were also measured in the nearby fly ash discharge basin and its associated drainage stream. Laboratory dissolution and precipitation studies of fly ash were performed in an effort to understand the chemistry of the discharged ash water and its potential effects on receiving waters. Mass balance calculations were made and are presented to ascertain whether the cooling pond acts as an efficent sink for inorganic and organic compounds, and if so, what the fate of these compounds is. Data presented in this report are also discussed in terms of plant operating characteristics. Remedial procedures are presented which could alleviate present and anticipated problems.

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SECTION 1

INTRODUCTION

Water utilization may, in many instances, place severe constraints on site selection and subsequent operational aspects of coal-fired steam plants. Various federal and state regulations require that the discharged water, whether it comes from cooling uses or fly ash disposal activities, be maintained at essentially the same quality as that of the receiving water. Maintenance of good water quality is not only desirable from an environmental viewpoint (that is, minimizing the release of hazardous substances), but is also important in the optimization of plant operations (see, for example, Sigma Research Report 1975). The latter point is especially germane where cooling ponds are present (Sams et al. 1978). It therefore becomes important to understand the various environmental factors that are involved in determining the water quality of these aquatic systems.

Similarly, the production of fly ash is, and will continue to be, a tremendous disposal problem. The annual discharge of individual elements in fly ash from coal-fired steam plants in the U.S. to landfills, fly ash basins, and other receiving waters has been compared to the mobilization of elements by natural processes, such as weathering (Klein et al. 1975). Table 1 indicates that elemental mobilization by fly ash ranges from 0.2 to 82% of the natural weathering products carried by U.S. rivers. The percentage will undoubtedly increase with the projected increase in coal utilization.

Since at one time or another the fly ash will come into contact with water, through disposal in either solid landfill, ash basin, or as soil amendment, study of the aqueous behavior of this material becomes important (Holland et al. 1975).

Few studies on the aquatic chemistry of cooling ponds exist in the literature, but an increasing amount of literature on the chemical composition of fly ash is now emerging. However, much more information is needed on the aqueous behavior of various fly ash materials, especially how this behavior relates to disposal questions.

The research presented in this report describes approximately 2 yr of detailed investigations of the aqueous chemistry of a 192-ha cooling pond and a 24-ha ash basin at the Columbia Generating Station near Portage, Wisconsin. The specific objectives were: (1) to compare water quality in the cooling pond to that of source waters and other Wisconsin lakes, (2) to estimate the amount of chemicals that annually reach the cooling pond and to relate this input to observed water concentrations, (3) to conduct

TABLE 1. COMPARISON OF ELEMENT MOBILIZATIONS BY WEATHERING AND FLY ASH DISPOSAL[a]

Element	Weathering mobilizations (x 10^3 tons/yr)	Fly ash disposal (percent of weathering)
Al	73,000	3
As	15	15
Ba	550	3
Br	34	0.2
Ca	42,000	2
Co	17	5
Cr	80	7
Cs	4	7
Fe	43,000	9
Hg	0.5	1
K	27,000	2
Mg	19,000	2
Mn	770	1
Mo	3.2	-
Na	18,000	1
Pb	22	7
Sb	4.3	4
Se	0.8	82
Si	75,000	8
Th	11	5
U	3.4	18
V	120	6
Zn	120	12

[a]From Klein et al. 1975.

laboratory experiments on fly ash dissolution, and (4) to compare laboratory experimental results with observed chemical parameters in a fly ash basin.

The first section deals with field measurements taken in the Wisconsin River and at selected sampling stations in the cooling pond. Concentrations of major, minor, and nutrient elements are discussed in terms of spatial and temporal variations. These data are then compared to similar data sets taken from Lake Mendota, Wisconsin, one of the best studied lakes in the world. The mechanisms responsible for maintaining the observed levels of chemicals in the cooling pond are then discussed in terms of a chemical equilibrium model. A model is also presented which predicts calcium carbonate precipitation (percent saturation) as a function of temperature and calcium concentration. This model was developed in an effort to provide plant operation guidelines since scaling problems in the cooling system sometimes present a severe problem.

The second major section deals with the chemistry of fly ash water interactions. Controlled laboratory studies were designed to evaluate the stoichiometry of liquid-solid phase reactions. Data from these measurements are then discussed in terms of various chemical models, where emphasis was placed on explaining the variables that control the dissolution and formation of major mineral phases. These results are then compared to field measurements from the ash basin.

Results from field and laboratory measurements are finally discussed in terms of environmental input on natural water systems. While much of this discussion deals with the Columbia Generating Station, it is nevertheless felt that the methodology used in this evaluation is transferable to other sites.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

Except for copper concentrations, the overall water quality of the cooling basin at the Columbia Generating Station is similar to that of many southern Wisconsin eutrophic lakes. Copper is elevated in the basin as a result of copper piping which is used for cooling purposes within the plant. Copper concentrations, however, are generally below those levels thought to be toxic to aquatic life. Because of evaporation, the conservative element concentrations (Na, K, SO_4, and Cl) in the cooling pond water generally are higher than those in source waters (the Wisconsin River). Although variable, this difference is usually 20 to 30%. Nutrient levels in the cooling pond are generally lower than those in the Wisconsin River (exceptions discussed below).

The cooling basin acts as a repository for a large fraction of the incoming non-conservative elements. That is, many of the nutrients and trace metals (whether in dissolved or particulate form) are removed from the water column by adsorption and settling.

Cooling basin bottom waters may turn anoxic during late summer, causing nutrients from bottom sediments to be released to the overlying waters. Low oxygen concentrations are common in both source and cooling pond waters during this period. Since nutrient release from bottom sediments to the water column may cause severe biological fouling problems, it is important to maintain oxygenated cooling pond waters at all times.

Because of elevated temperatures and relatively high alkalinity values, the cooling pond water is usually supersaturated with calcium carbonate. This condition is most severe in late summer and can cause severe scaling problems within the plant's cooling system. The most effective remedy appears to be frequent blowdowns during this period.

Cooling pond water contained non-detectable levels (less than 7 to 10 ng/liter) of chlororganics and polyaromatic hydrocarbons. Bottom sediments contained measurable quantities of chlorinated phenols, phthalate esters, and polyaromatic hydrocarbons. The source of the latter is thought to be windblown coal dust from the nearby coal storage area. While polyaromatic hydrocarbon and chlororganic analyses of fish caught in the cooling basins are not yet available, PCB concentrations were similar to those found in fish collected from non-contaminated lakes.

Results from laboratory studies on dissolution and precipitation reactions of fly ash during equilibrium conditions can not be directly extrapolated to the ash basin at the Columbia Generating Station. The short residence time of water and intermittent fly ash input places kinetic constraints on the system. However, results from laboratory studies and chemical equilibrium modeling were extremely valuable in our attempt to understand *in situ* control mechanisms.

Major element chemistry determines the reaction mechanism of fly ash dissolution by establishing solid-solution metastable equilibria. Dissolved calcium and magnesium concentrations are controlled by their carbonate and hydroxide solid phases. Aluminum and iron hydroxide phases control their dissolved concentrations in appropriate pH regions. Silica appears to exist mainly as an amorphous phase but also may be incorporated in an aluminosilicate phase at mid-pH values. Hydrolytic dissolution of Ca, Mg, Na, and K are responsible for high pH values observed both in laboratory experiments and in the ash basin waters. However, atmospheric CO_2 entering the solution will lower the pH at steady-state conditions. The isoelectric pH (the pH where the particles in aqueous suspension contain a net zero charge--pH_{IEP}) of Columbia fly ash is approximately 7.55, which also indicates that Fe and Al dominate the solid phase reactions at mid-pH values.

Dissolved Cd concentrations at high pH values suggest that this element precipitates as hydroxide and carbonate phases. Below pH 9.0 adsorption reactions most likely control its dissolved concentrations. Dissolved P concentrations are stongly influenced by adsorption reactions between pH 4.5 and 8.5. Phosphorous most likely precipitates as a hydroxyapatite phase at higher pH values. Co-precipitation of P with Ca and Mg probably also occurs above pH 10. Other trace cations and anions behave in an analogous manner.

Elevated concentrations of Al, B, Cd, and Cu are present in the ash basin at levels deemed toxic to aquatic life. In addition, pH values are always in the range of 9 to 12, most of the time less than 11.0.

Elemental mass-balance calculations in the ash basin indicate that the major fraction of elements discharged into the basin remain in the system (except Na and SO_4). Although ions such as Al, Cr, B, As, and Se might be hazardous to biota, elemental discharge from the ash basin has a negligible effect on the water quality of the Wisconsin River, with the possible exception of Na, B, and Cr. The concentration changes in the river, however, cannot be measured *in situ* because they are less than the standard deviation of analytical precision. Thus, any biological effect that results in the discharge of chemicals from the ash basin should be confined to the drainage ditch.

Diversion of ash basin effluent into the cooling pond may lead to several possibilities. Several elements are present in concentrations above recommended water quality criteria. However, less than 40% of the water in the cooling pond would come from this source. The only elements of potential concern would then be SO_4, B, and Al. Aluminum would rapidly precipitate and possibly aid in removing part of the suspended sediments in

the cooling pond. Further information is required concerning average ash basin B concentrations. However, even after dilution, this element could be present in significant concentrations. Sulfate would not directly be a problem in the cooling pond after dilution. However, potential anaerobic conditions in the cooling pond could lead to H_2S generation. After Na_2CO_3 had been added to improve the efficiency of the electrostatic precipitator, Ca and CO_3 concentrations in neutralized ash basin discharge waters were often below concentrations present in the cooling pond. Thus, diversion may partially alleviate the scaling problems in the plant. Some evidence indicates that Al precipitation is enhanced once the ash basin water is neutralized. Use of one of the current ash basins or construction of an additional settling basin for receiving the neutralized effluent may tremendously decrease total Al and adsorbed species discharges.

Although no environmentally significant concentrations of ash basin contaminants have been observed in the surrounding groundwater at this time, we believe that further study is necessary. Currently, modeling is impractical because of the need for additional hydrogeological information. This is particularly needed with respect to the amount of leachate infiltrating directly through the ash basin dike and remaining on the surface of the sedge meadow. Additionally, current wells may not be directly intersecting ash basin infiltrate and new plastic wells may be required before subsurface water movements can be adequately described. Monitoring well water and ash basin dissolved element concentrations during an extended period of steady-state flow would aid in developing a representative model. Information concerning soil composition (cation exchange capacity, organic matter, clay, $Fe(OH)_3$, $Mn(OH)_4$, and SiO_2 content) would also be required if adsorption modeling is attempted.

The periodic monitoring of existing wells surrounding the ash basin should continue. In addition, samples of stagnant water bodies adjacent to the ash basin should also be included in the sampling regime. If groundwater concentrations exceed accepted water quality criteria, maximum ash basin pumping (with consequent increased infiltration) could be delayed until heavy rainfall and melting snow dilute surface and subsurface water contaminants.

SECTION 3

METHODS

EXPERIMENTAL PROCEDURES USED IN THE MONITORING STUDY

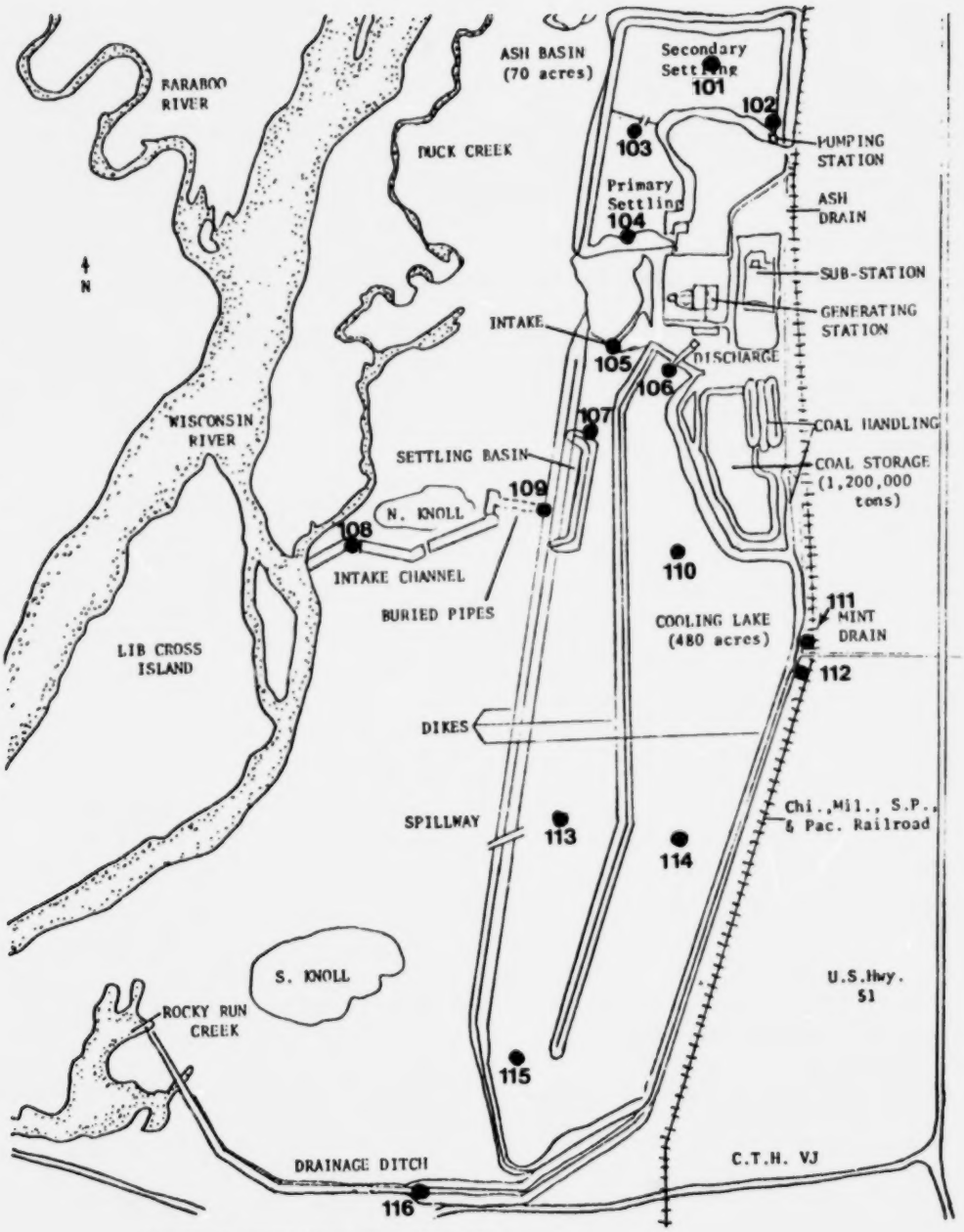
The Columbia Generating Station, located on the Wisconsin River in south-central Wisconsin, consists of two nearly identical 527-MW units. Columbia I went into operation in May 1975 and Columbia II in April 1978. During the period of the monitoring study, Columbia I was burning high ash, low sulfur coal from Montana.

Figure 1 shows the locations of the sampling stations where water samples were collected at 1-month intervals from June 1976 to April 1977. Wisconsin River water is pumped to the 192-ha (480-acre) cooling pond through the ditch and underground pipes located west of the pond. Although cooling water is not directly discharged from the cooling pond into the Wisconsin River, during periods of blowdown water flows through a spillway into a sedge meadow surrounding the plant. Fly ash is flushed into the settling basins with cooling pond water obtained at the plant intake. Fly ash leachate eventually reaches the Wisconsin River by way of the drainage ditch depicted on the right and bottom of Figure 1.

Table 2 lists a water balance for average daily flow through the site. Pumping records, temperature data, and well levels outside the ponds were used by the hydrogeology subproject of the Columbia impact study to derive these estimates of water flow. The cooling pond circulation time averages 5 days and the hydraulic residence time approximately 80 days. The depths of the cooling and ash ponds vary. However, the maximum depth at any station is limited to 3 m. Further details on water flow around the power plant, including flow characteristics and geomorphology, can be found in Anderson and Andrews (1976).

A Kemmerer water sampler was used to collect all water samples and 2-liter polyethylene bottles were used for storage. Nucleopore (0.4 μm) membrane filters were used for filtration. Trace metal samples were preserved by adding 2 ml of redistilled nitric acid (16) per liter of sample. The September 1976 suspended solid samples were analyzed by neutron activation analysis on preweighed 0.45 μm Millipore filters dried at 80°C.

All polyethylene and glass containers used during collection and analyses were washed with hot 50% hydrochloric acid (10% nitric acid for trace element storage bottles) and rinsed several times with distilled water and sample solution.



COLUMBIA GENERATING STATION SITE.

Figure 1. Location of sampling stations at the Columbia Generating Station.

Table 3 lists the analytical procedures used in the study. In most cases, determinations were performed utilizing techniques detailed in Standard Methods for the Examination of Water and Waste Water (American Public Health Association 1971, 1974). Calcium and magnesium analyses were performed by adding of lanthanum to prevent refractory compound formation during flame atomic adsorption. All flameless and most flame atomic adsorption analyses were performed on a Perkin Elmer model 603 Atomic Adsorption Spectrophotometer equipped with an HGA 2100 graphite furnace. Dissolved oxygen and temperature analyses were performed on site with a Yellow Springs Instrument dissolved oxygen meter. The instrument was precalibrated several times using the Winkler dissolved oxygen technique and laboratory thermometer. The carmine spectrophotometric procedure for boron was performed using a standard additions procedure. X-ray diffraction analyses of ash basin sediment samples were performed using a mounting procedure described by Gibbs (1965).

The three stations located at the intake channel and in the preliminary settling basin (Figure 1) were used to evaluate the chemical characteristics of incoming Wisconsin River water. Single samples were collected at the intake and discharge stations depicted on the map. At all stations inside the cooling and ash basins, water samples were obtained at surface, mid-depth, and bottom.

From June to October 1976, 28 monthly water samples were collected, filtered, and analyzed for 15 parameters. In November, three stations (110, 113, and 114) were deleted from the monitoring schedule since variations in dissolved element concentrations in the cooling pond were minimal. Sulfate and nitrogen analyses were discontinued at that time, and total dissolved phosphorus, aluminum, cadmium, chromium, copper, and iron were added to the list of measured elements. In September 1977, a short-term intensive sampling of the ash basin was instituted with an overall design of evaluating sedimentation in the ash basin in addition to estimating dissolved concentrations of arsenic, lead, zinc, and boron.

The results presented in this report are reduced to average values and ranges in elemental concentrations observed at the sampling stations. Appendix A provides specific details regarding precision of analyses and raw data obtained during the period of study.

EXPERIMENTAL PROCEDURES USED IN THE LABORATORY LEACHING STUDY

Composite samples of fly ash used in the laboratory experiments include: (1) fly ash collected underwater off the end of the ash delta (submerged), (2) freshly deposited fly ash on the ash delta (wet delta), (3) fly ash deposited on the ash delta but dewatered (dry delta), and (4) fly ash from stages II and III of the electrostatic precipitator hopper bins (5 September 1975). Samples 1, 2, and 3 were collected from the ash delta at locations indicative of various stages of leaching by pond waters or rainfall. After collection, each composite sample of fly ash was air dried at room temperature (20°C) and subsequently sieved through a U.S. Standard 325 sieve. The fly ash fraction collected from sieving consisted of

TABLE 2. AVERAGE DAILY WATER FLOW AT THE COLUMBIA GENERATING STATION[a]

Daily flow (m^3/day)	Source	Destination
5.4×10^4	Wisconsin River	Cooling pond
1.1×10^4	Cooling pond	Spillway
2.1×10^4 [b]	Cooling pond	Groundwater
1.2×10^4	Cooling pond	Ash basin
1.0×10^4 [b]	Cooling pond	Atmosphere (evaporation)

[a] Anderson and Andrews (1976).
[b] Estimates, Anderson and Andrews (1976).

TABLE 3. ANALYTICAL PROCEDURES USED IN THIS STUDY

Element	Procedure	Reference
Alkalinity	Titrimetric	Standard Methods (1971)[a]
Aluminum	Flameless atomic absorption	Perkin Elmer (1975)[b]
Boron	Carmine-Spectrophotometric	Standard Methods (1971)
Cadmium	Flameless atomic absorption	Perkin Elmer (1975)
Calcium	Flame atomic absorption	Standard Methods (1974)[c]
Chloride	$AgNO_3$-CrO_4	Standard Methods (1971)
Chromium	Flameless atomic absorption	Perkin Elmer (1975)
Copper	Flameless atomic absorption	Perkin Elmer (1975)
Iron	Flameless atomic absorption	Perkin Elmer (1975)
Lead	Flameless atomic absorption	Perkin Elmer (1975)
Magnesium	Flame atomic absorption	Standard Methods (1974)
Nitrate	Cadmium reduction	Standard Methods (1974)
Nitrite	Sulfanilamide-Spectrophotometric	Standard Methods (1974)
Oxygen	Yellow Springs Instrument probe	
pH	Glass electrode	Standard Methods (1974)
Phosphorus	Phosphomolybdate-Spectrophotometric	Standard Methods (1974) Eisenreich et al. (1975)
Potassium	Flame atomic absorption	Standard Methods (1974)
Silica	Molybdosilicate-Spectrophotometric	Strickland and Parsons (1968)
Sodium	Flame atomic absorption	Standard Methods (1974)
Sulfate	Turbidimetric	Standard Methods (1974)
Temperature	Yellow Springs Instrument probe	
Zinc	Flame atomic absorption	Perkin Elmer (1975)

[a] American Public Health Association (1971).
[b] Perkin (1975).
[c] American Public Health Association (1974).

particles less than 44 μm in diameter. Drying of the sieved fly ash was completed in a dessicator where the samples were stored until use.

Duplicate equilibrium leaching experiments were conducted in large polyethylene containers. A solid-solution ratio of 1 g ash/liter of doubly distilled water was utilized for each fly ash sample. These slurries were stirred for several months at a constant rate using electric stirrers equipped with polyethylene blades. At selected time intervals, an aliquot was removed from each slurry and the pH was measured with a low junction potential electrode (Sargent Welch Model S-30072-25). Each aliquot was then filtered through a prewashed 0.4 μm Nuclepore filter, and the filtrate was divided for elemental analysis. Dissolved aluminum (Okura et al. 1962), dissolved reactive phosphorus (Murphy and Riley 1962), and dissolved reactive silica (Strickland and Parsons 1968) were determined colorimetrically from one fraction. The remaining filtrate was acidified to 0.5% nitric acid for later analysis by atomic absorption spectroscopy (Perkin Elmer Model 603) for Ca, Cd, Fe, K, Mg, and Na. Solids collected on the Nuclepore filters were subjected to analysis by X-ray diffraction.

During electrophoretic mobility measurements large volumes of fly ash slurries were prepared using the same four fly ash samples. A constant solids concentration of 200 mg/liter was used to facilitate zeta potential measurements. The slurries were stirred for 1 week to obtain pH stability. At this time, 12 aliquots from each slurry were dispensed into 250 ml linear polyethylene bottles (LPE). The pH was adjusted from 1.0 to 12.0 with perchloric acid or potassium hydroxide. These slurries were then shaken at a constant temperature (20°C) for 1 additional week. The final pH was recorded and the electrophoretic mobility was determined with a lazer-Zee Meter (Pen-Ken, Inc.). The remaining slurry was filtered and elemental analyses were conducted on the filtrate as previously described. All field samples were filtered in the same manner so that dissolved concentrations could be compared directly with those determined in these laboratory experiments.

Each fly ash sample was subjected to wet digestion to obtain values for the total concentration of major and minor elements. A satisfactory method was developed for digesting 25 mg of fly ash in a LPE bottle below the boiling point of hydrofluoric acid (112°C). This technique minimized silica loss by volatilization as fluoride compounds, a major problem associated with the decomposition of inorganic siliceous materials (Langmyhr and Paus 1968). The LPE bottles containing the fly ash and acids (HNO_3, HCl, and HF) were placed on a hot sand bath at 100°C $\pm$ 3°C for digestion. After cooling, the solution was diluted and elemental analysis was performed by colorimetry or flame atomic absorption spectroscopy. Duplicate sample digestions were conducted five times. Calculations of individual elemental recoveries are based on analyses of NBS Standard Fly Ash #1633 using the digestion technique described above.

SECTION 4

CHEMICAL CHARACTERISTICS OF THE COLUMBIA COOLING LAKE

The initial investigation at the site of the Columbia Generating Station examined the water quality in the Columbia cooling lake. The primary objective of this study was to determine the major processes influencing water quality in the Columbia cooling basin. Potential hazards and suggestions for minimizing possible problems were evaluated by comparing cooling lake water with data on water quality characteristics from the Wisconsin River and selected southern Wisconsin lakes. In addition, a computer program was used to predict elemental speciation and saturation in the cooling lake.

LITERATURE REVIEW

The early literature concerning water quality of power plants deals primarily with water treatment practices required for plant maintenance. These practices included addition of toxic compounds (e.g., Hg, Zn, Cr, B, and Cu salts) and complexing agents (e.g., phosphates and organic compounds such as EDTA) for prevention and minimization of fouling and scaling problems. A recent concern about water quality degradation in discharge waters caused by these additives was reported by Chamberlain and Anderson (1971). These authors suggested the use of ion exchange resins for removing zinc-organic inhibitors from discharge waters. Stratton and Lee (1975) found elevated concentrations of nitrate, phosphate, sulfate, zinc, iron, copper, chromium, and mercury in cooling tower blowdown water. Concentrations of manganese, nickel, and cadmium were not sufficiently high to be of environmental concern. The authors attributed most of the elevated concentrations to chemicals used in water treatment.

In recent years several reports have addressed the environmental impact of cooling systems on aquatic environments. A report by Sigma Research (1975) recommended the development of models for the realistic evaluation of power plant operation on biota. In particular, the authors were concerned about the effects of sublethal chlorination. Anderson and Smith (1977) reported increased mercury concentrations in cooling basin sediments after power plant operation, although similar elemental increases were not observed in fish. Sams et al. (1978) used a holistic approach to determine the relationship between the chemistry of a cooling reservoir and its source water. Using background data and information from samples obtained during the study period, the authors observed a progressively increasing concentration of major elements in the reservoir (presumably through evaporative concentration). At the same time, levels of nutrients decreased and concentrations of dissolved reactive phosphorus, total phosphorus,

dissolved reactive silica, and iron typically were lower than concentrations observed in the source water. Dissolved oxygen ranged from 5 to 11 mg/liter, except for sporadically low values observed during the summer. Concentrations of potentially toxic trace elements (chromium, copper, lead, and zinc) were near or below the analytical detection limit. The authors concluded that: (1) dissolved solids increased by a factor of 3 to 7; (2) phosphorus was precipitating with iron and calcium; and (3) the environment was becoming less suitable for autotroph production.

One may infer from these reports that drastic alterations in the water quality of cooling basins are not to be expected in the absence of toxic additives. Evaporative concentration may exert a significant effect on the biotic communities only when exceptionally high concentrations of dissolved solids occur. The elevated water temperature present in cooling basins may accelerate biological processes and may limit the dissolved oxygen concentrations during the summer months.

RESULTS AND DISCUSSION

A comparison of parameters at various stations in the cooling pond at the Columbia Generating Station indicated that the water circulation period was sufficiently short to preclude horizontal and vertical gradients for any of the elements determined. Figure 2 illustrates a surface temperature gradient in the cooling pond for September 1976. This profile is typical for periods when the plant is operational. Surface and bottom elemental concentrations demonstrate that the cooling pond is ordinarily well mixed. Except for a period in August 1976, when bottom oxygen levels were low and dissolved reactive phosphorus concentrations were high, all surface, mid-depth, and bottom samples contained roughly equivalent elemental concentrations.

Average concentrations of calcium, magnesium, sodium, potassium, chloride, sulfate, and alkalinity invariably remained higher in the cooling pond than in the Wisconsin River (Figure 3). In addition, a gradual trend toward higher concentrations was observed at the end of the sampling period. These factors indicate evaporative concentration. Magnesium, sodium, and chloride display reasonably similar time profiles and may be regarded as conservative elements. The anomalous relationship between the river and the cooling pond for sodium and chloride in January 1977 may possibly be explained as a short-term phenomenon caused by road salt application during the winter months.

When compared with major elements, nutrient behavior is much more variable and concentrations in the cooling basin normally are lower than those in Wisconsin River water (Figure 4). The dissimilarities in the behavior of major elements and nutrients indicate that predictive modeling for the nutrients is difficult. For major elements predictive modeling is relatively straightforward if evaporation rates are known. The most significant nutrient variations occur during August when bottom water oxygen levels approached the detection limit. At this time, total and dissolved reactive phosphorus concentractions increased by a factor of 100. This suggests that phosphorus is retained in the sediments with iron. The

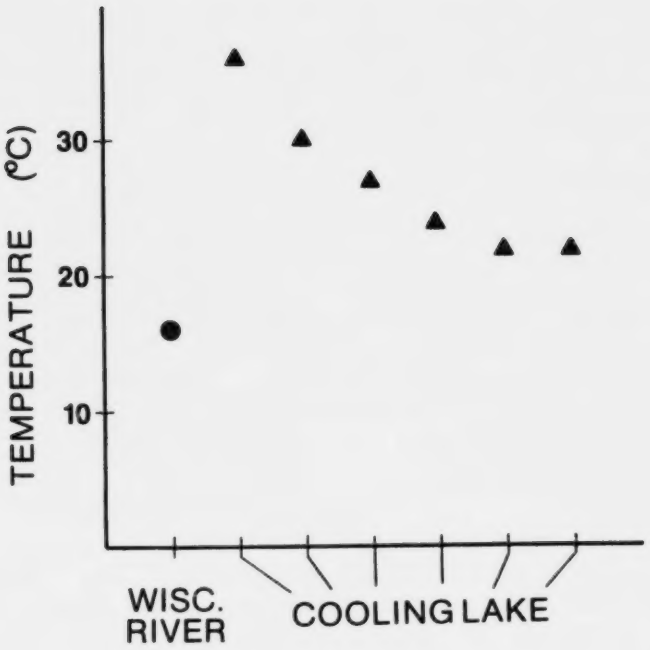


Figure 2. Temperature profile at various stations in Wisconsin River and cooling lake waters (obtained September 1976).

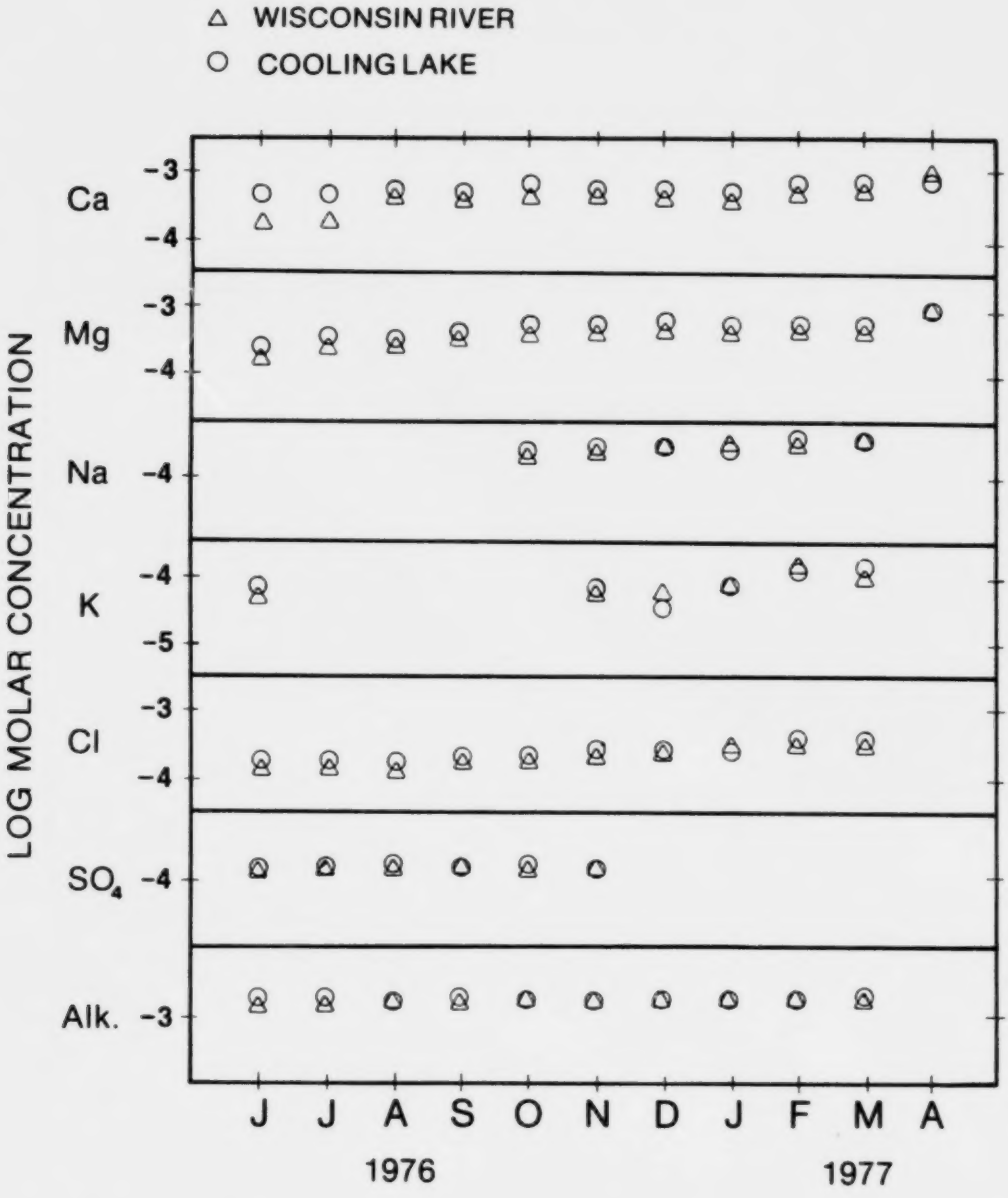


Figure 3. Average monthly nutrient concentrations in Wisconsin River and cooling lake waters. (Dotted lines depict detertion limits.)

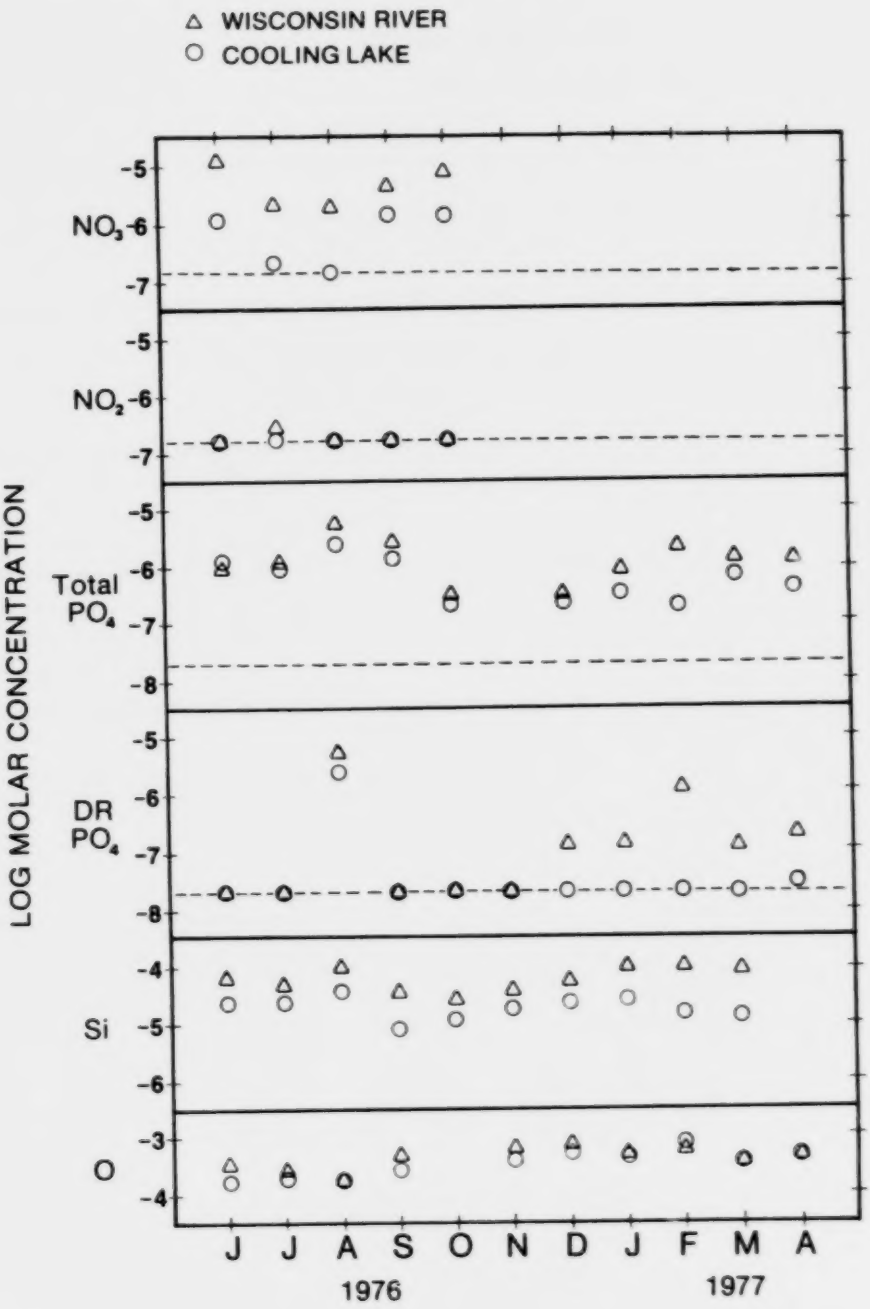


Figure 4. Average monthly major element concentrations in Wisconsin River and cooling lake waters.

release of phosphorus during $Fe(OH)_3$ reduction has been demonstrated by numerous investigators (for example, Syers et al. 1973) and will not be discussed here. Other indications of possible reducing conditions can be observed in the nitrate and nitrite profiles in Figure 4. Bacterial reduction may explain the lower nitrogen concentrations associated with the elevated phosphorus levels. The maximum in dissolved reactive silica in the fall of 1976 may also be explained by biological activity since diatom growth exerts significant effects on soluble silica in other Wisconsin lakes (Vigon 1976).

Major element concentrations in the cooling pond were compared in Table 4 with concentrations observed in Lake Mendota, one of the most thoroughly studied lakes in the world. In almost all cases, the ranges in concentrations are remarkably similar. The most significant difference appears to be the temperature maximum observed in the cooling pond. However, closer inspection of the nutrient concentrations yields additional insight into processes occurring within the cooling basin. The dissolved reactive phosphorus concentrations in the cooling pond, considerably lower than in Lake Mendota, are often near the detection limit of 0.003 mg/liter. This may indicate a limiting nutrient status. Total phosphorus concentrations observed in both bodies of water lead to their classification

TABLE 4. CONCENTRATIONS OF MAJOR ELEMENTS IN THE COLUMBIA COOLING POND AND LAKE MENDOTA

Element	Concentrations observed in cooling pond (mg/liter)	Concentrations observed in Lake Mendota[a] (mg/liter)
O_2	0-15	0-15
Ca	28-36	26-30
Mg	10-20	23-28
Na	7-12	4.5-8.0
K	1.8-2.0	3.5-4.0
NO_3	<0.01-0.10	<0.01-0.7
NO_2	<0.01-0.02	0.0025-0.02
Total P	0.03->1.7	0.05-0.65
Ortho P	<0.003-1.7	0.02-0.40
Ortho Si	0.1-1.6	0.1-1.5
Cl	9-19	6.2-9.6
SO_4	12-19	18-30
Alkalinity[b]	117-142	140-193
pH	6.6-8.2	6.5-9.2
Temperature (°C)	0-37	0-27

[a]Unpublished data, Water Chemistry Program, Univ. of Wisconsin-Madison (1965).
[b]Expressed as mg/liter $CaCO_3$.

as eutrophic lakes (Vollenweider 1968). A comparison of seasonal distributions of total phosphorus in the cooling pond with those observed in Lake Mendota (Sonzogni 1974) illustrates a late fall maximum for epilimnetic water in Lake Mendota in contrast to the summer maximum observed in the cooling pond. Since the cooling pond is normally well mixed, its chemical and physical characteristics approach those of epilimnetic water in a stratified lake. The presence of a hypolimnion isolates the epilimnion from sediment interactions until fall overturn. In contrast, the water in the cooling pond is immediately influenced by sedimentary processes. Since anoxic conditions in the sediments are more likely to occur in the summer when the temperature is high and wind action low, a maximum amount of phosphorus will be released to the water during this season. Additionally, since the sediment-water interactions are normally confined to the upper few inches of the sediment, then the speed and magnitude of a response will show an inverse dependence to volume of water in the overlying column. Piwoni (1974) examined the nutrient concentrations in 10 shallow manmade impoundments in south-central Wisconsin. The author observed higher and more variable median summer dissolved phosphorus concentrations in these lakes when compared to a larger body of water. In summary, the cooling pond and other shallow basins will experience an immediate response to sediment conditions, and the magnitude of the responses will be inversely dependent on the depth of the basin.

The range and average values for trace elements in the cooling pond were also compared with these values in the Wisconsin River waters (Table 5). For all elements except copper, cooling pond concentrations are equal to or lower than those found in the source water. Comparison of copper concentrations at plant intake and discharge demonstrates that the plant is a significant source of this element in the system. Copper concentrations are often twice as large in discharge waters. The most plausible source for

TABLE 5. TRACE ELEMENTS IN THE COOLING POND AND THE WISCONSIN RIVER

	Cooling Pond		Wisconsin River	
Element	Range (mg/liter)	Average (mg/liter)	Range (mg/liter)	Average (mg/liter)
Al	0.003 - 0.080	0.027	0.027 - 0.102	0.056
Cd	<0.0001 - 0.0003	<0.0001	<0.0001 - 0.0001	<0.0001
Cr	<0.001		<0.001 - 0.001	<0.001
Cu	0.002 - 0.011	0.008	<0.0003 - 0.002	0.001
Fe	<0.01 - 0.12	0.10	0.22 - 0.52	0.35
Pb	<0.002		<0.002	
Zn	<0.005		<0.005 - 0.010	0.010
B	<0.1		<0.1	

increased copper concentrations is from within the plant because soluble copper values decrease when the plant is not operational.

Data for soluble aluminum and iron indicate that both elements are precipitating in the cooling basin. The concentration differences between the cooling pond and source water suggests that the majority of these elements remain in the sediments of the cooling pond. The concentrations of all trace elements are well below water quality recommendations, although copper concentrations approached 0.020 mg/liter on several occasions, an upper limit suggested by Van Hook and Shuttts (1976).

A computer program was used as an aid to determine whether selected dissolved elements exceed their solubility product. Table 6 presents the results obtained from the MINEQL computer program designed to solve simultaneous equilibrium equations (Westall et al. 1976). Using average values of cooling pond concentrations, an ionic strength of $6x10^{-3}$, a constant pH of 8.0, and neglecting redox and adsorption reaction (assuming oxygenated water), the program generated a prediction of thermodynamic equilibrium concentrations for a variety of elements. The second column in Table 6 represents the initial molar concentration of dissolved elements and succeeding columns display the predicted final equilibrium percent distribution of soluble species and precipitates. Three species, $Fe(OH)_3$, $Al(OH)_3$, and $CaCO_3$ are predicted to precipitate in the basin. Although copper concentrations decline when the plant ceases operation, no insoluble compound is predicted. Presumably, the rate of plant input is balanced by the rate of biological assimilation or inorganic adsorption of copper onto sedimenting particles in the basin (when the plant is operational). The majority of the trace elements (assuming no adsorption) have not exceeded solubility constraints. Therefore, for accurate modeling, a subroutine must be added to the program to account for adsorption reactions.

Problems with scaling have been reported at the Columbia plant (WPL personal communication 1977), particularly in late summer. Figure 5 illustrates the saturation of calcium carbonate with temperature assuming constant pH (8) and alkalinity (120 mg/liter). This figure was derived from the equations and temperature-dependent formation constants listed in Table 7. An increase in temperature from 20 to 35°C or a calcium concentration of 20 mg/liter results in potential precipitation of one-half the soluble calcium. Obviously, the solubility of calcium carbonate is sensitive to temp rature as well as pH and alkalinity. Scaling problems may be minimized only .y decreasing one of these three variables. An average cooling pond calcium concentration of 30 mg/liter demonstrates that calcium carbonate is supersaturated at any of the temperatures listed in Figure 5, which is consistent with MINEQL calculations based on formation constants at 25°C. Predictions of the formation of this compound in the cooling pond, in addition to within the plant, are thus possible. Although these calculations have not been corrected for ionic strength, this effect would be minimal. Figure 5 can thus be utilized as a reasonably accurate predictive tool for saturation of calcium carbonate in the cooling pond.

TABLE 6. MINEQL COMPUTER PROGRAM RESULTS FOR AVERAGE CONCENTRATIONS OBSERVED IN THE COOLING POND (25°C)

Element	Initial concentration[a]	Soluble species	%	Precipitate	%
Ca	9.06×10^{-4}	Ca^{++}	60.1	$CaCO_3$	36.1
		$^{+}CaHCO_3^{+}$	2.2		
		$CaSO_4$	1.0		
Mg	7.49×10^{-4}	Mg^{++}	92.2		
		$MgHCO_3^{+}$	3.4		
		$MgSO_4$	2.0		
		$MgCO_3$	1.4		
K	4.30×10^{-5}	K^{+}	99.9		
Na	3.41×10^{-4}	Na^{+}	99.9		
Cu	1.42×10^{-7}	$CuCO_3$	93.2		
		$Cu(CO_3)_2^{-2}$	2.6		
		$Cu(OH)^{+}$	2.2		
		Cu^{++}	2.0		
Cd	8.90×10^{-10}	Cd^{++}	87.4		
		$Cd(OH)^{+}$	7.4		
		$CaCl^{+}$	2.4		
		$CdSO_4$	1.5		
		$CdCO_3$	1.3		
SO_4	1.84×10^{-4}	$SO_4^{=}$	87.0		
		$MgSO_4$	8.0		
		$CaSO_4$	4.9		
Cl	3.81×10^{-4}	Cl^{-}	100.0		

(continued)

TABLE 6 (continued)

Element	Initial concentration[a]	Soluble species	%	Precipitate	%
SiO_4	1.42×10^{-5}	H_4SiO_4	97.1		
		Al H_3SiO_4	2.9		
PO_4	4.16×10^{-8}	$HPO_4^=$	73.4		
	13.3	$H_2PO_4^-$			
		$MgHPO_4$	10.6		
		$CaHPO_4$	2.6		
Fe	1.61×10^{-6}			$Fe(OH)_3$	100.0
Al	9.27×10^{-7}	$Al(OH)_4^-$	2.5	$Al(OH)_3$	97.5
CO_3	2.46×10^{-3}	HCO_3^-	82.1	$CaCO_3$	13.3
		H_2CO_3	1.4		
		$MgHCO_3$	1.0		

[a]Total molar dissolved cooling pond concentrations.

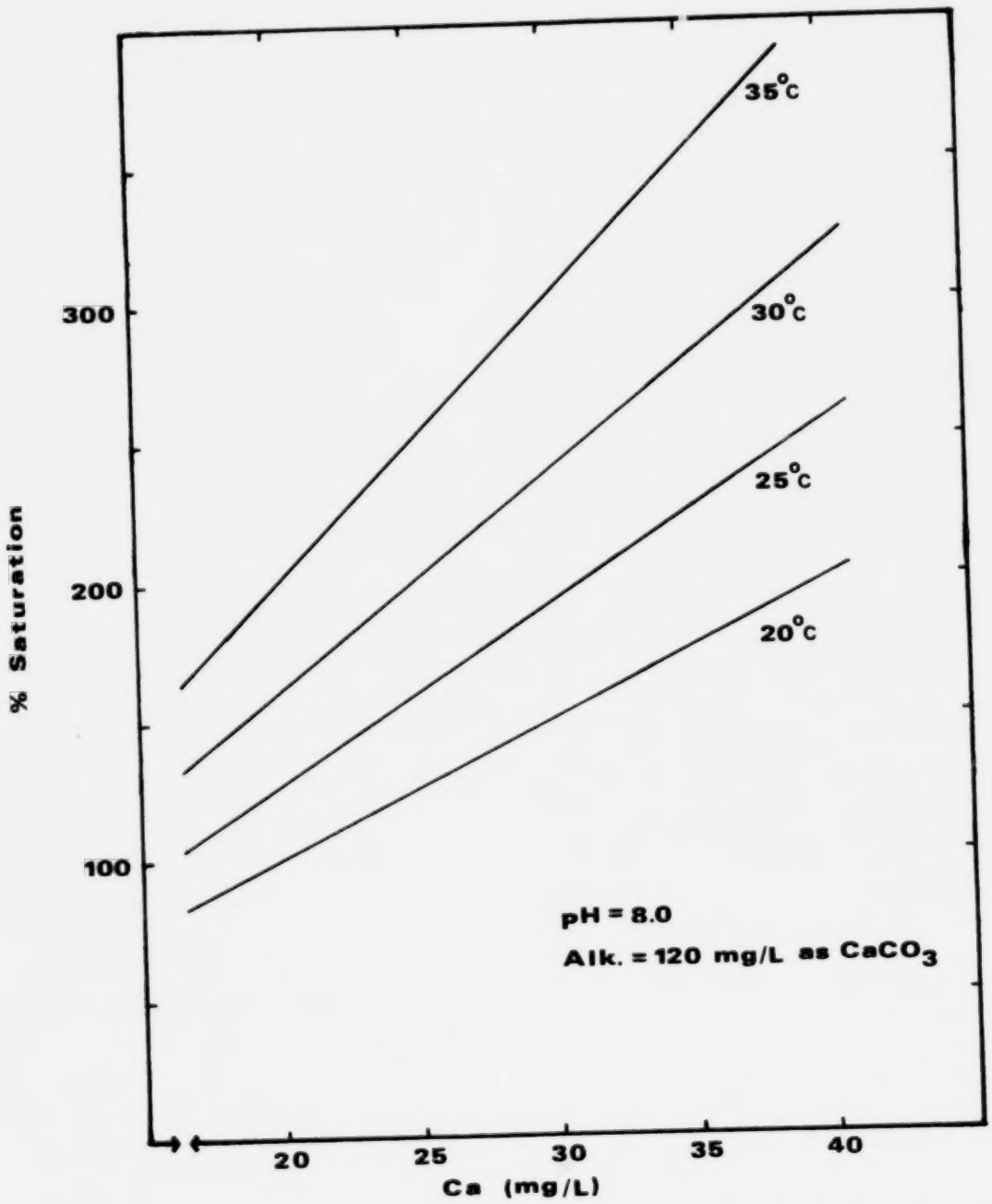


Figure 5. Calcium carbonate saturation in the cooling lake as a function of dissolved calcium concentration at various temperatures.

TABLE 7. EQUATIONS AND FORMATION CONSTANTS USED IN CONSTRUCTING FIGURE 5

Equations

$$[TA] = \frac{\text{Measured alkalinity}^{a}}{50,000}$$

$$[CO_3] = \frac{[TA]\ K_2}{[H^+] + 2\ K_2}$$

$$[Ca^{++}] = \frac{\text{Ca concentration (mg/liter)}}{40,080}$$

$$K_{sp} = [Ca^{++}]\ [CO_3^{=}]$$

$$\% \text{ saturation} = \frac{[Ca^{++}]\ [CO_3^{=}] \times 100}{K_{sp}} = [Ca^{++}]\left(\frac{[TA]\ K_2}{[H^+]+2K_2}\right)Ksp^{-1} \times 100$$

Formation constants[b]

Temperature (°C)	K_2	K_{sp}
20	4.17×10^{-11}	5.25×10^{-9}
25	4.68×10^{-11}	4.57×10^{-9}
30	5.13×10^{-11}	3.98×10^{-9}
40	6.02×10^{-11}	3.02×10^{-9}

[a] The effects of conjugate bases other than carbonate are minimal on the total alkalinity measurements.
[b] Garrels and Christ 1965.

Suspended solids in both cooling pond and the Wisconsin River waters ranged from 8 to 15 mg/liter for the samples obtained during the study. Table 8 displays elemental concentration ratios for several sparingly soluble elements present in suspended sediments obtained during September 1976. Since total quantities of suspended sediments in the cooling pond and Wisconsin River were equivalent, ratios ranging from 2 to 3 imply a fractionation of inorganic sediments once the source water enters the cooling pond. The majority of the sediments entering the system appear to deposit in the bottom of the cooling basin. Biogenic material generated within the cooling pond then replaces the fraction lost from sedimentation.

TABLE 8. ELEMENTAL RATIOS FOR SELECTED ELEMENTS IN SUSPENDED SOLIDS

Element	Wisconsin River to Cooling Pond elemental ratios for suspended solids
Co	2.0
Hf	2.7
La	2.8
Lu	2.8
Rb	1.8
Sb	2.3
Sc	3.1
Sm	3.0
Tb	2.7

SECTION 5

ORGANIC CONTAMINANTS IN COOLING POND SEDIMENTS

Welch (1979) has recently received our present knowledge on coal burning related organic chemicals. He concluded that aromatic hydrocarbons, particularly the polyaromatic hydrocarbons (PAH), should receive particular attention. John and Nickless (1977) found several PAH in river sediments downstream from a coal mining area (Table 9). Waditer and Blackwood (1978) also found that PAH could leach from coal storage areas (Table 9). These observations prompted Welch (1979) to analyze sediments for both chlorinated and nonchlorinated PAH in cooling pond sediments at the Columbia Power Generating Station. The coal storage area adjacent to the cooling pond has a capacity of about 1,200,000 tons. It was postulated that part of the coal becomes windborne and will subsequently settle into the cooling basin. It was also postulated that these PAH, if present in the sediments, would become chlorinated because of rather efficient chlorination of discharged cooling water. Sediments were thus collected approximately 25 m from the cooling water discharge using a power dredge. The sediment was stored in pre-cleaned glass bottles with Teflon-lined caps.

Details of the analytical procedure has been published by Welch (1979). Briefly, dry sediment was soxhlet extracted with methylene chloride for 5 days. The extract and solvent was then dried (anhydrous sodium sulfate), evaporated, and filtered (Whatman No. 2). The filtered solution was finally evaporated to dryness, weighed, and dissolved in circa 15 ml benzene. Sulfur was removed using freshly precipitated copper. The solution was again evaporated to dryness and subsequently taken up in 0.5 ml of a 1:1 methanol-benzene mixture. This fraction was then cleaned using gel permeation chromatography, evaporated to dryness, and finally taken up in 0.5 ml acetonitrile. This sample was then fractionated using HPLC and finally analyzed with a Finnigan 4023A GC/MS/DS system. No recovery studies were performed. The results must therefore only be considered in a qualitative sense.

The sediment (155 g, dry weight) yielded approximately 33 mg of extractable organic material. The specific compounds are identified in Table 9. No chlorinated PAH were found. As a matter of fact, very few PAH were found. While several other PAH undoubtedly are present, they are below the limit of detection. The same technique was used to identify aromatic hydrocarbons in the Duluth-Superior Harbor. Over 60 aromatic compounds were identified including about 40 PAH and their alkylated homologs. Several chlorinated biphyenyls were also identified. Most aromatic compounds, if present in the Columbia cooling lake, are thus quite low in concentration.

TABLE 9. AROMATIC HYDROCARBON COMPOUNDS IDENTIFIED IN THE COLUMBIA COOLING BASIN[a]

Compound	M+	Other ions[d]
Methylethylbenzene[b]	120	105, 91, 77
Dimethylnapthalene[b]	156	141, 128
Dichlorothiazolopyrimidine[c]	205	207, 209, 170, 172
Phenanthrene	178	152, 89
Tetrmethylphenanthrene	234	219, 204

[a] From Welch (1979).
[b] Exact structure not determined.
[c] Tentatively identified.
[d] GC/MS conditions: 2 mm x 1.8 m glass column with 3% OV-1 on 60/80 Gas Chrom Q; temperature program 100-225°C/4°/min, initial hold 1 min.; Finnigan 4023A scanned 50-500 amu at 2.0 sec/scan, started at time of injection.

SECTION 6

CHEMICAL CHARACTERISTICS OF THE COLUMBIA FLY ASH BASIN

The second major area of inquiry at the Columbia Generating Station was concerned with the identification of the potential hazards associated with fly ash disposal in an impoundment pond. Two approaches were developed for meeting this objective: (1) Controlled laboratory leaching studies designed to evaluate the stoichiometry of liquid-solid phase reactions and (2) on-site measurement of major and selected trace element concentrations. The mobilization of potentially toxic elements is limited by adsorption and/or precipitation reactions on solid phases present in the ash basin. Therefore, before a theoretical model for elemental mobilization can be generated, these solid phases must be characterized in terms of their mineral composition and their surface charge properties. The mineral composition must be assessed because of the possibility of co-precipitation of environmentally significant trace elements, and the surface charge properties are significant because of their profound influence on adsorption reactions. After it was determined that soluble element concentrations for major and minor elements were controlled by solid phase reactions, both the laboratory leaching and the on-site monitoring studies focused on solid phase identification.

Identification of potentially toxic concentrations of various elements was achieved in the on-site measurement study. However, a theoretical prediction of behavior (especially for trace constituents) cannot be derived because all thermodynamically stable solid phase reactions have not been definitively identified. Kinetic studies will be required once the appropriate processes have been determined.

LITERATURE REVIEW

The previous literature on fly ash leachate may be divided into five categories. The first area, typified by toxicity studies by Reese and Sidrok (1956) and Holliday et al. (1958), demonstrated that elevated concentrations of Al, Mn, and B in fly ash leachate may be toxic to aquatic life. These studies were concerned primarily with observing elemental concentrations and identifying the parameters limiting optimum biotic development. A second area of inquiry concerned the pozzolanic characteristic of fly ash and the suitability of using the material as a filler concrete. Brink and Halstead (1956) examined the matrix composition of several types of fly ash and determined the potential extractable components under varying leaching conditions. A third area of study concerns laboratory leachate studies investigating major and trace element mobilization and its possible relationship to initial matrix composition.

Jones and Lewis (1960), Shannon and Fine (1974), Natusch (1975, 1976), Theis and Wirth (1977), and Eggett and Thorpe (1978) demonstrated elevated concentrations of SO_4, Ca, Mg Na, K, Si, Al, B, Fe, Cd, Cu, Hg, Cr, Zn, H, and OH in fly ash leachate and attempted to determine correlations between elemental mobilization and the physical and chemical characteristics of the fly ash. Studies by Tenny and Echelberger (1970) and Higgins et al. (1976) illustrate the fourth area of inquiry which concerns the suitability of using fly ash for treatment of eutrophic lakes. Both studies characterized short-term elemental fluctuations in terms of the fly ash leachate and adsorption of phosphorus and organic material from water derived from eutrophic lakes. The final area of study is exemplified by more recent studies concerning elemental mobilization with attendant environmental degradation at several power station fly ash disposal sites located in the United States. Cherry et al. (1976) demonstrated biological magnification of several potentially toxic elements in aquatic organisms at a power station in South Carolina. Coutant et al. (1978) described solid and soluble phase chemical compositions at several sampling sites in a drainage ditch adjacent to a power plant in Tennessee. Theis and Richter (1978) documented the impact of fly ash leachate on the groundwater at a power station near Lake Michigan.

Previous site-specific studies on the interaction of fly ash with water have focused mainly on the chemical composition of the leachate. Although such studies are useful it is also important to keep in mind that the solid phase determines subsequent aqueous interactions. The present literature does not contain enough information that specifically relates the chemical composition of the total phase (that is, mineral phase composition) to that of expected elemental concentrations in the leachate. As a first approximation, the potential environmental impact of fly ash disposal is limited by the characteristics of the parent coal. Extreme variations in pH (from acidic to basic) and soluble major and minor element compositions in fly ash leachate have been observed in the literature. Such variations make it very difficult to predict the environmental impact of fly ash and indicates that a better understanding of aqueous interactions can only be made by combining detailed field and laboratory studies.

LABORATORY LEACHING EXPERIMENTS

Equilibrium leaching experiments of fly ash in water were included as part of the aquatic chemistry study since adequate information describing those processes that control the chemical composition of ash pond waters is not available. These systems provide an environment in which certain trace elements may be leached from impounded ash then enter groundwaters by infiltration, receiving waters through direct ash pond discharge, and the surrounding land area via runoff.

The results obtained by previous investigators do not provide a basis for defining the geochemical processes ultimately responsible for controlling the distribution of major, minor, and trace elements between dissolved and particulate phases. This investigation was directed toward identifying and describing important geochemical processes that determine the metastable equilibrium conditions established in this complex

heterogeneous system. Consequently, considerable emphasis was placed on delineating the geochemistry of major (Al, Fe, Si) and minor (Ca, Mg, Na, K) constituents of fly ash. These elements were chosen for study since they represent major components of Columbia fly ash (Helmke et al. 1976, Talbot 1977). Furthermore, these elements are known to exert extremely important controls on the trace element distribution of natural water systems (Schindler 1967, Garrels and Mackenzie 1977, Stumm and Morgan 1970). A more complete understanding of the heterogeneous processes involving these elements should facilitate the interpretation of the trace element distribution and behavior. Such information is required before the fate of elements entrained in this system can be determined. An estimate of the amount available for transport to uncontaminated natural ecosystems would then be possible. This approach to studying the ash pond chemistry provides a basis for interpreting similar data collected at other ash pond sites. Although environmental conditions and ash composition vary, similar major solid phases are expected to be formed. The relative proportions, and in some cases the overall importance, of these various phases, are probably influenced most by the parent ash composition.

RESULTS

The fly ash used in this investigation can be described as a collection of heterogeneous particles that are principally spherical in shape. Each ash particle is composed of a suite of elements contained in a glassy amorphous matrix. Table 10 presents the total elemental concentration of each Columbia fly ash sample. An empirical formula:

$$Si_{0.769}Ca_{0.294}Al_{0.233}Mg_{0.156}Fe_{0.059}K_{0.012}Na_{0.009}$$

was calculated using values obtained from total digestion of the hopper fly ash. These fly ash samples thus appear to have an aluminosilicate

TABLE 10. TOTAL ELEMENTAL CONCENTRATIONS OF COLUMBIA FLY ASH EXPRESSED AS PERCENTAGE OF DRY WEIGHT

Element	Submerged	Wet delta	Dry delta	Hoppers
Al	6.3	5.7	6.5	6.3
Ca	11.4	11.7	11.2	11.8
Cd	<0.001	<0.001	<0.001	<0.001
Fe	3.0	2.7	3.2	3.3
K	0.46	0.40	0.43	0.45
Mg	3.4	3.4	3.5	3.8
Na	0.26	0.34	0.28	0.21
P	0.12	0.13	0.12	0.11
Si	23.0	20.6	22.4	21.6
Zn	0.0020	0.0019	0.00021	0.00017

structure. However, the presence of a well-defined mineral phase is unlikely because the composition of the samples is complex. Other investigaters have postulated that many trace elements are contained as condensed species surrounding the ash particle (Davison et al. 1974, Linton et al. 1976). The exact mechanism of attachment to the ash particle is still unknown as is the chemical form(s) of the trace elements.

Once the fly ash particles contact an aqueous environment, solid phase dissolution reactions occur immediately. Figure 6(a-i) illustrates the dissolution as a function of leaching time for several major and minor elements in fly ash. Sharp increases in dissolved aluminum, iron, and silica concentrations are clearly indicated. In addition, the largest amount of Al, Ca, Fe, Mg, Na, and Si is leached from the hopper ash which had not been exposed previously to water. The dissolution of these elements is probably enhanced by the rise in solution pH (Figure 7). Aluminum, iron, and silica are particularly soluble at elevated pH values. The release of these elements to the dissolved phase (Figure 6a-c) clearly concurs with the dramatic increase in pH shown in Figure 7. Hydrolysis of oxide forms of Ca, K, Mg, and Na are suspected to cause the initial pH increase. Shannon and Fine (1974) attribute the high pH of water extracts collected during fly ash leaching to the hydrolytic reactions of these elements; for example,

$$CaO + H_2O = Ca^{+2} + 2OH^- \quad \text{and} \tag{1}$$

$$Na_2O + H_2O = 2Na^+ + 2OH^- \tag{2}$$

Analogous reactions may also be written describing the hydrolysis of carbonate forms of these elements. However, magnesium oxides are essentially inert (Cotton and Wilkinson 1972) and therefore are not expected to be appreciably hydrolyzed. Magnesium entering the bulk solution at this time is most likely associated with soluble calcium or magnesium compounds other than the oxide.

All four fly ash slurries stabilized at nearly the same pH value after 1 week of leaching. This indicates that the processes controlling pH were the same in all cases regardless of any previous leaching the ashes may have undergone. Figure 8 shows that the same pH trend with time was observed when the experiment was conducted under a nitrogen atmosphere to exclude atmospheric CO_2 from the system. Several weeks elapsed before the pH declined to lower values. The pH decrease in the open systems after 1 or 2 h apparently resulted from diffusion of atmospheric CO_2 into this highly alkaline medium. Only 9×10^{-11} moles of CO_2 per hour would typically be required in each instance to lower the pH from its higher value to its level at 48 h into the experiment. This diffusion rate, however, only considers neutralization of OH^- species. Since silica ($H_3SiO_4^-$) and other anionic species (for example, $Al(OH)_4^-$ may also accept H^+ as the pH decreases, a somewhat higher diffusion rate than calculated here might be required.

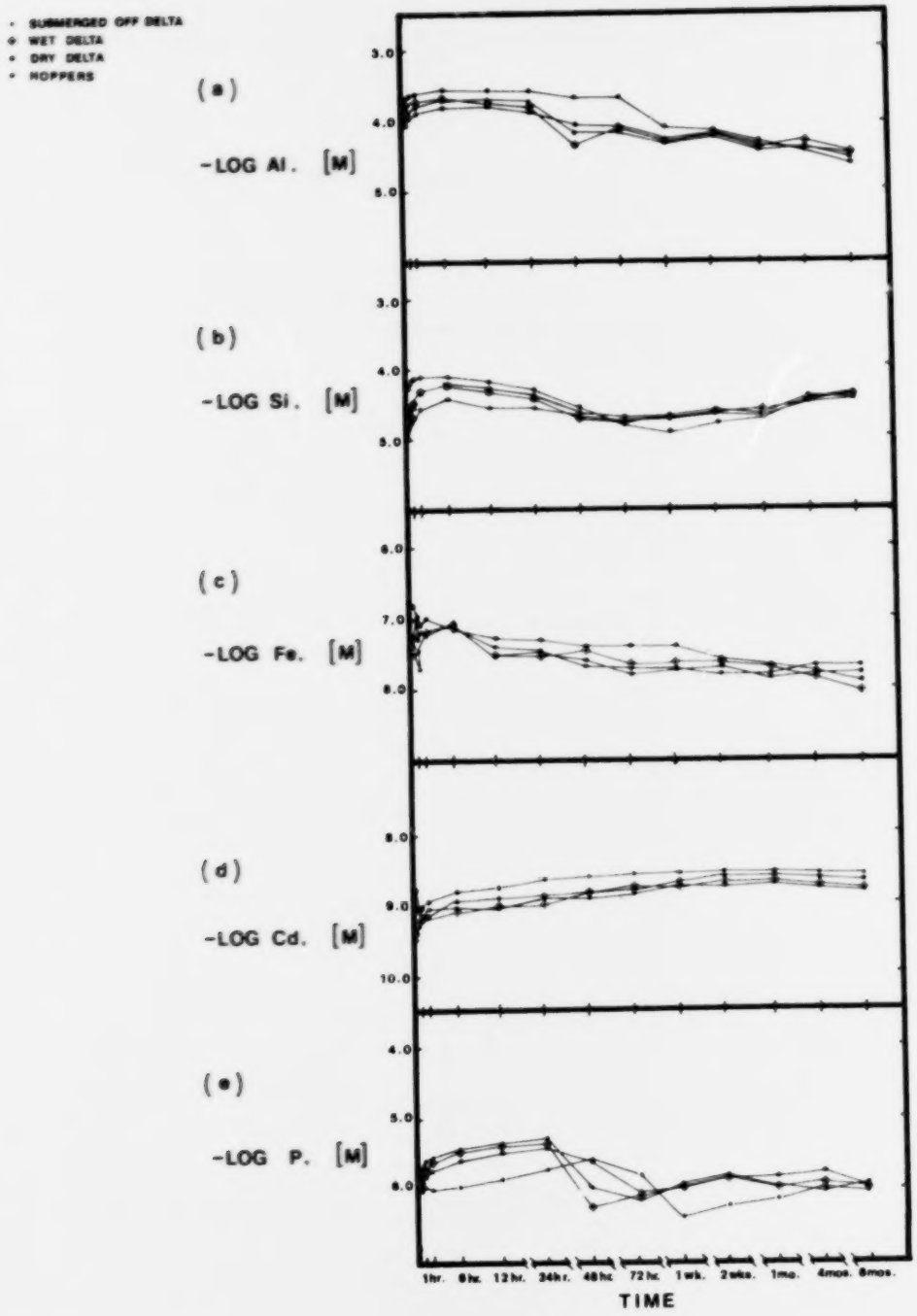


Figure 6(a-e). Change in dissolved elemental concentrations as a function of leaching time. (continued)

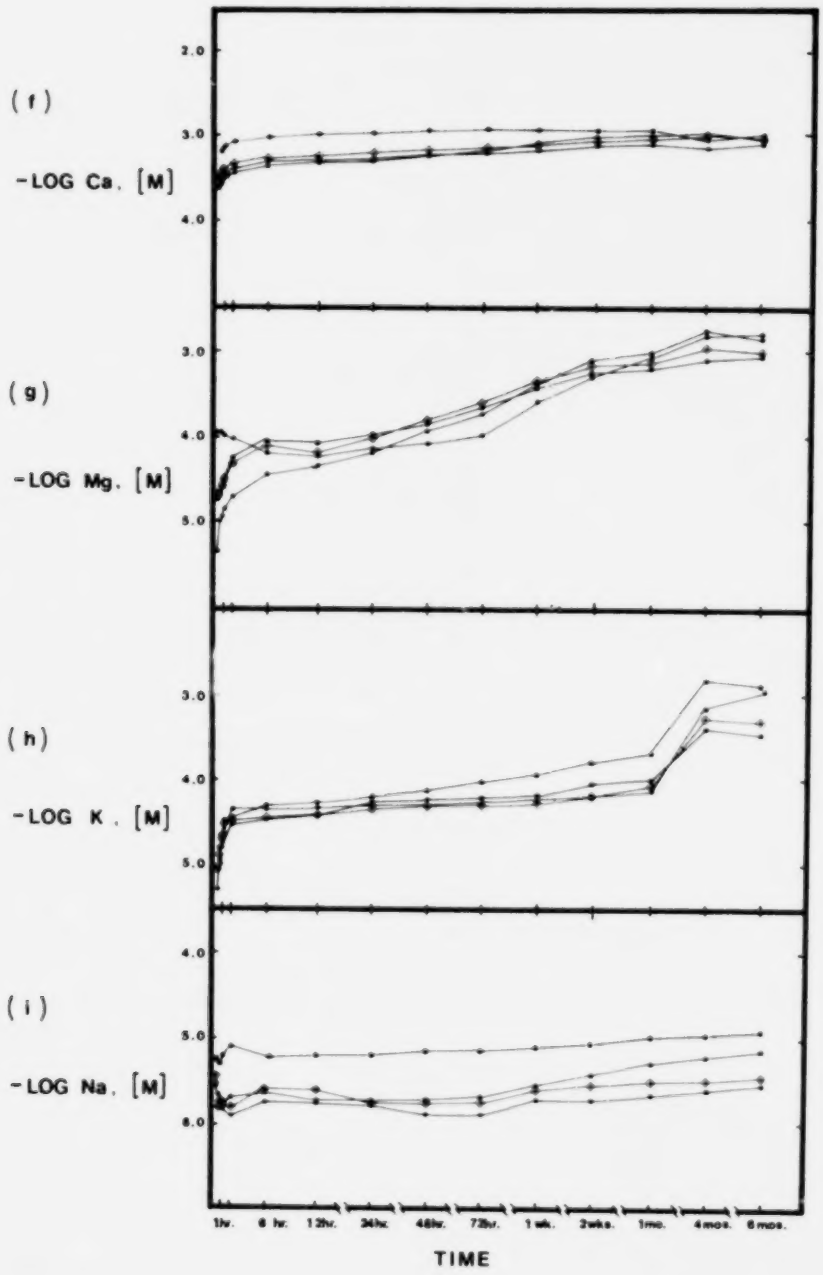


Figure 6(f-i). Change in dissolved elemental concentraitons as a function leaching time.

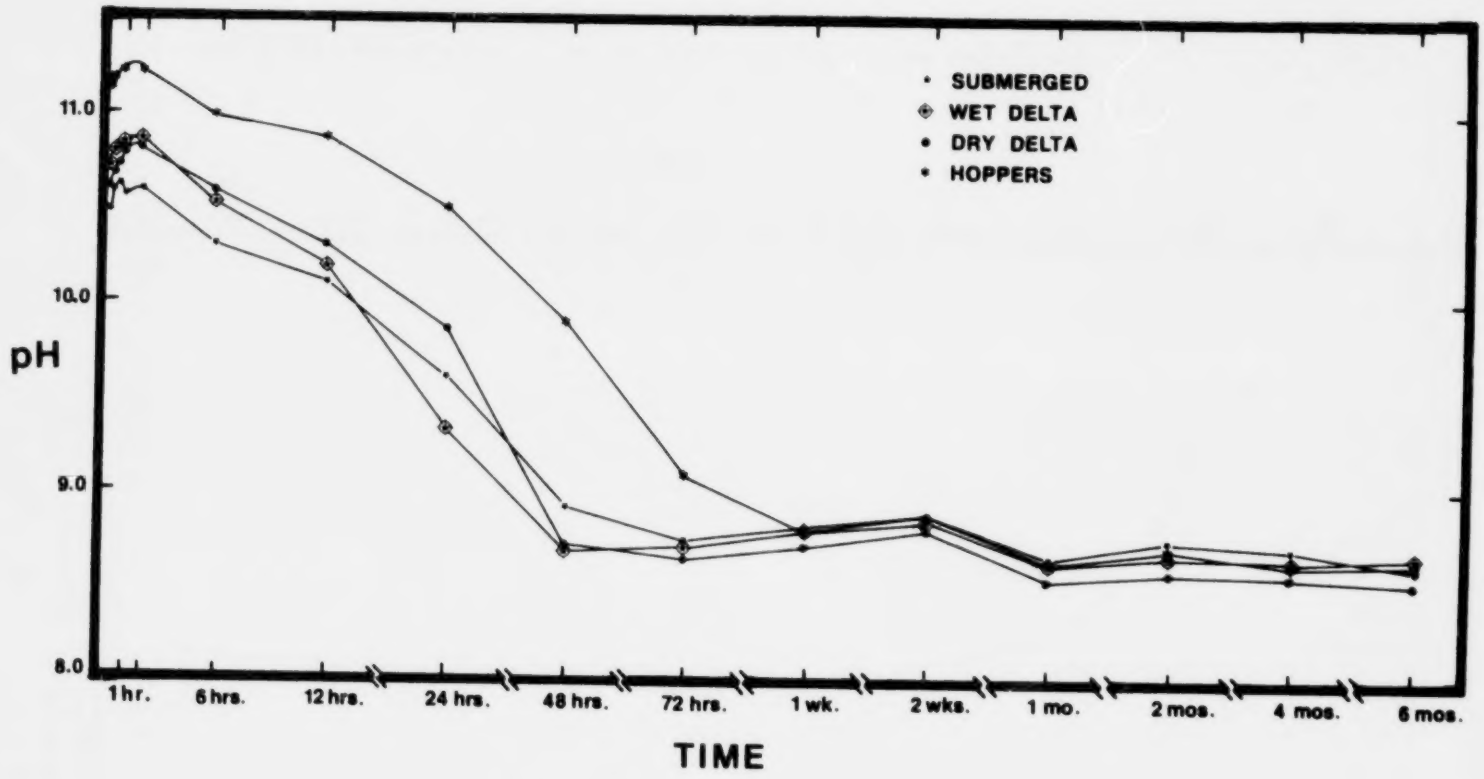


Figure 7. Change in pH with leaching time in system open to the atmosphere.

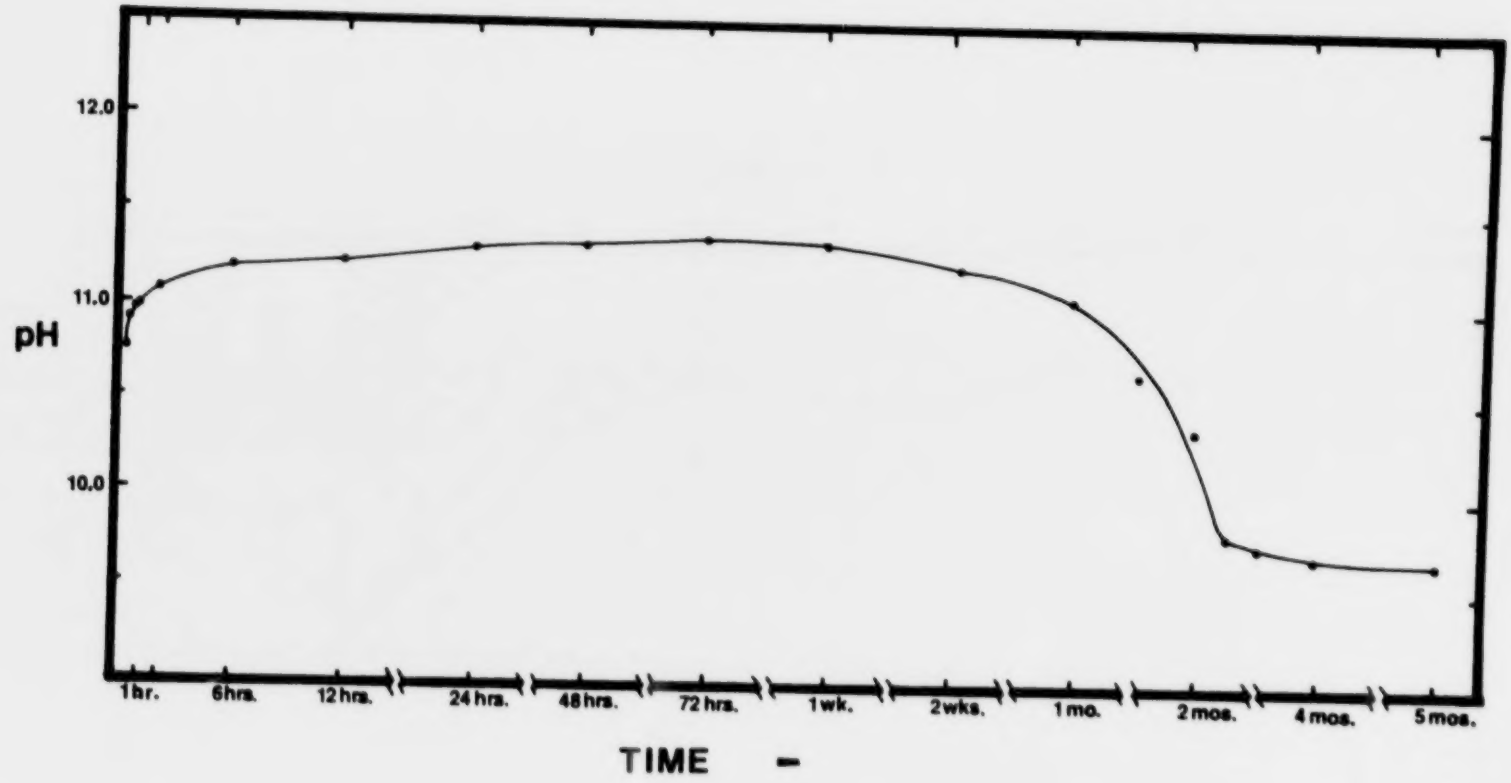


Figure 8. Change in pH with leaching time in system closed to the atmosphere.

Although the actual amount of CO_2 consumed cannot be calculated, the atmosphere can easily supply the necessary amount based on the above estimation.

Aluminum and Silica--

The heterogeneous reactions involving aluminum and silica provide a basis for understanding the metastable equilibrium conditions that determine the stability of fly ash in an aqueous system. The release of aluminum and silica to the bulk solution as a function of the square root of time ($t^{1/2}$) is depicted in Figure 9. The change in dissolved concentrations of aluminum and silica with time have been divided into three stages to aid the interpretation of their heterogeneous reactions. The rate constants (K) for dissolution of aluminum and silica from the fly ash during stage 1 can be calculated from their respective slopes. The value of K was found to be 3.70×10^{-5} moles l^{-1} hour $^{-1/2}$ for aluminum and 1.83×10^{-5} moles l^{-1} hour $^{1/2}$ for silica. Hence, aluminum enters the bulk solution approximately twice as fast as silica. This ratio suggests that additional dissolution reactions (for example, $Al_2O_3 + 5H_2O = 2Al(OH)_4^- + 2H_+$) may be occurring for aluminum in addition to those corresponding to dissolution of an aluminosilicate phase.

The amount of aluminum compared to the amount of silica that precipitates during stage 2 implies that an aluminum-rich phase must form. The solubility of amorphorus aluminum hydroxide is exceeded 2.6 times as stage 2 commences, which strongly suggests that aluminum is precipitating as hydrous aluminum oxide or gibbsite. Co-precipitation and adsorption processes most likely account for the concurrent decline in dissolved silica. In addition, formation of an aluminosilicate mineral phase may be occurring to some extent.

The dissolved silica concentration at $t^{1/2}$ = 12.96 h or 3 days (log K_{SO} = -4.93) is below that necessary (log K = -4.70) to maintain stability of an aluminosilicate phase such as kaolinite with respect to gibbsite. Therefore, the gradual decrease in dissolved aluminum during stage 3 is attributed to formation of an aluminum oxide phase. This phase is probably formed by precipitation from the bulk solution as the pH decreases, and partly by the incongruent reaction:

$$Al_2Si_2O_5(OH)_{4(s)} + 5H_2O = Al_2O_3 \cdot 3H_2O_{(s)} + H_4SiO_{4(aq)} \qquad (3)$$

The gradual increase in dissolved silica agrees with this reaction. These solid phase rearrangements are still apparently occurring after 6 months of equilibration caused by the slow reaction kinetics of aluminosilicate minerals and a downward pH trend favoring gibbsite stability. Hence, these phases are expected to form in the ash pond if the pH is allowed to decrease by decreasing or stopping the continuous input of fly ash.

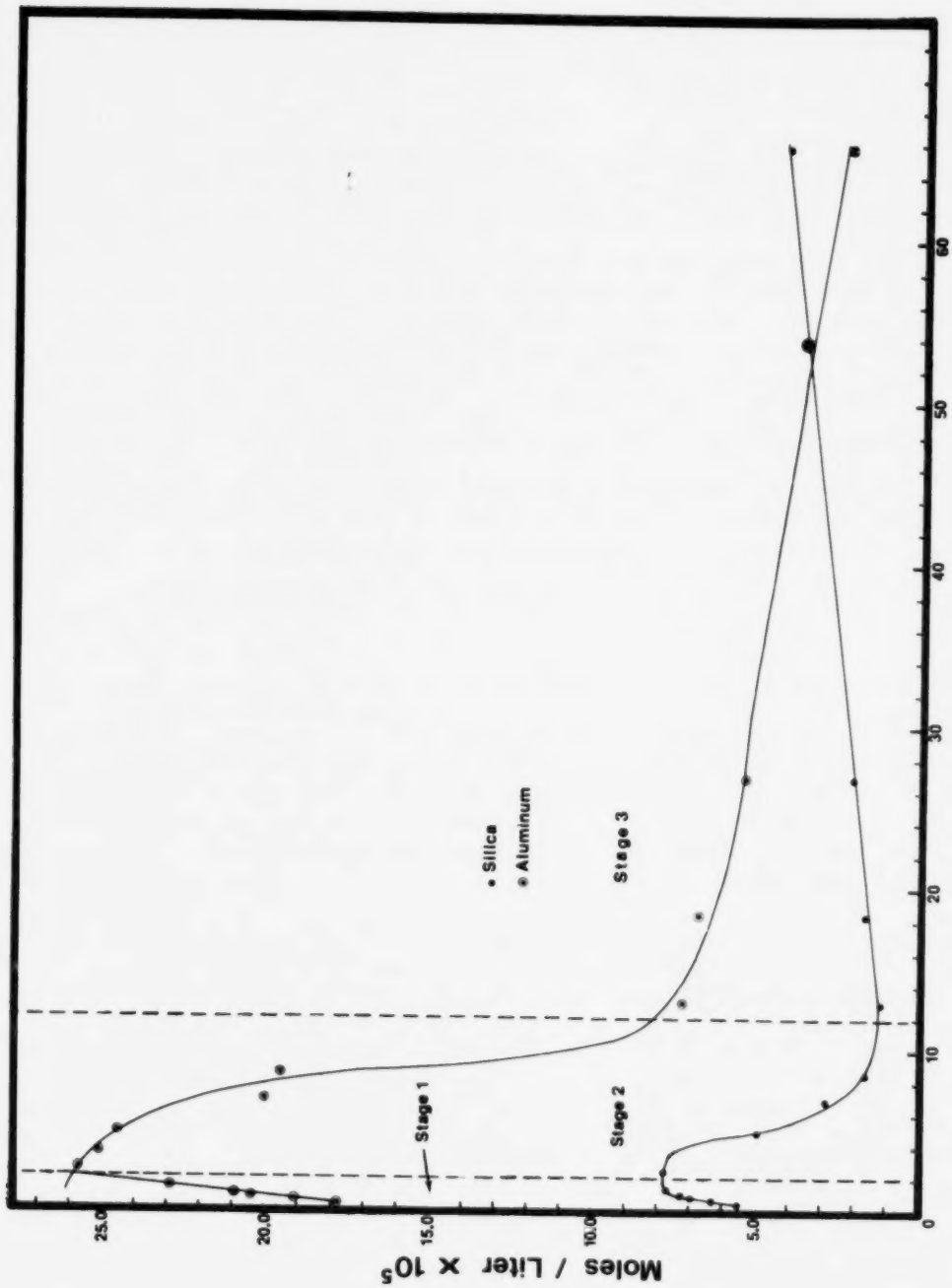


Figure 9. Dissolved aluminum and silica as a function of the square root of leaching time.

The phases forming during stage 3 are also predicted by the plots of dissolved aluminum and silica versus pH. These plots are shown in Figure 10a and b. The abrupt decrease in dissolved aluminum between pH 4.5 and 8.5 clearly coincides with the pH region where hydrous aluminum oxide is most stable (Parks 1972). In several samples from this pH region, microcrystalline gibbsite was identified by X-ray diffraction analysis. However, the principle phase is probably amorphous aluminum oxide. The slopes of the lines between pH 4.5 to 6.5 and 6.5 to 8.5 for aluminum in Figure 10a (that is, -3.3 and +2.0, respectively) are much steeper than would be expected from equilibrium relationships of hydrous aluminum oxide with corresponding aqueous aluminum species. This result implies that Figure 10a demonstrates only the presence of an aluminum phase in the pH region where aluminum is virtually insoluble in an aqueous system. If equilibration times at each pH value had been longer the pH dependence of aluminum would most likely be more consistent with that of a hydrous aluminum oxide system.

The decreasing dissolved silica concentrations between pH 12.3 and 4.3 (Figure 10b) may reflect the specific adsorption of silica onto the hydrous aluminum oxide phase, since this behavior is not expected by reaction (Eq. 3). Thus, this apparent adsorption may suppress the dissolution of silica if the ash particles encounter natural waters. Silica in the bulk solution below pH 4.3 concurs with the disappearance of the aluminum phase. Silica that enters the dissolved phase below pH 4.3 is apparently derived solely from the aluminosilicate structure of the fly ash. The nearly constant molar ratio of dissolved aluminum and silica, below pH 4.3 (Al)/(Si) = 1.10, is further evidence that only the aluminosilicate structure of the fly ash is dissolving.

The existence of an aluminosilicate phase over the entire pH range was confirmed by X-ray diffraction analysis. Unfortunately, these diffraction patterns are not distinct enough to allow deduction of an exact composition or structure. Since the Al/Si ratio in the original fly ash samples most likely includes aluminum and silica associated with other phases (for example, amorphous silica and aluminum oxides), the dissolved aluminum and silica concentration at pH 4.3 was used to estimate their ratio in the parent aluminosilicate phase. This pH value appears to represent a pH region where incongruent dissolution or adsorption reactions do not alter the aluminosilicate solubility. The calculated Al/Si molar ratio of 1.0 is similar to the ratio that would result from the congruent dissolution of a mineral phase similar in composition to kaolinite. If this aluminosilicate phase is represented by kaolinite, its solubility can then be calculated according to the reaction

$$Al_2Si_2O_5(OH)_{4(s)} = 6H^+ = 2Al^{+3} + 2H_4SiO_{4(aq)} + H_2O \qquad (4)$$

The solubility relationship of this phase at equilibrium can be expressed as:

$$K_{SO} = \frac{(Al^{+3})^2 \ (H_4SiO_4)^2}{(H^+)^6} = -\Delta 6^0 f/RT \quad (5)$$

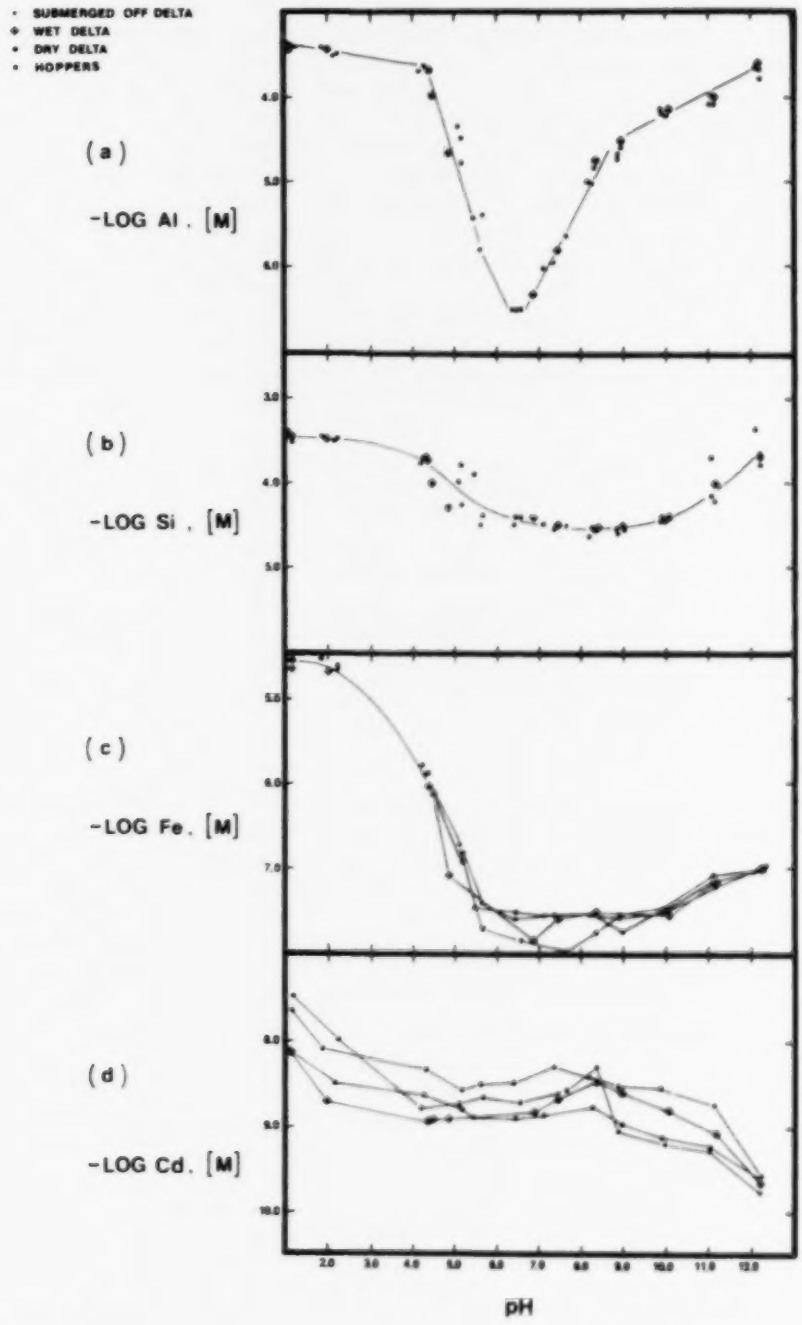


Figure 10(a-d). Dissolved elemental concentrations as a function of pH. (continued)

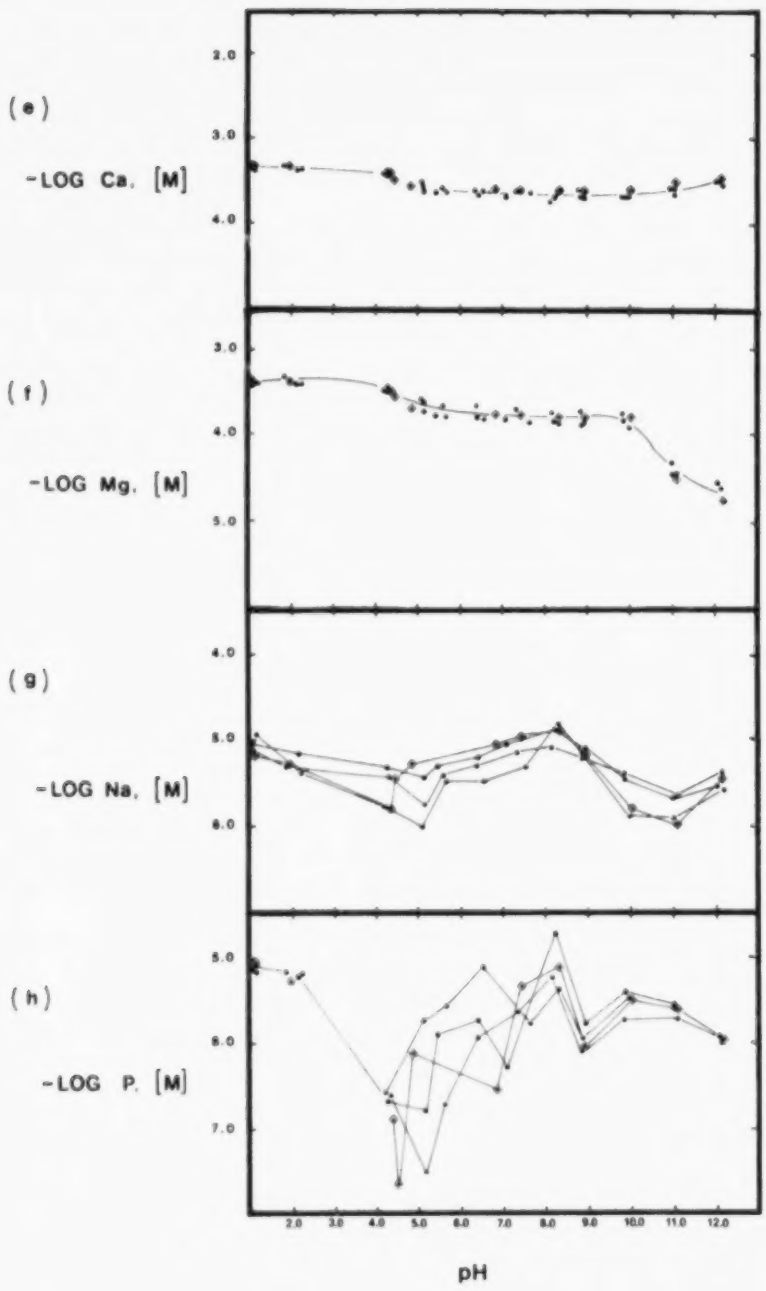


Figure 10(e-h). Dissolved elemental concentrations as a function of pH.

where log K_{SO} = 11.28 (Hem et al. 1973). Using dissolved aluminum and silica concentration at pH 4.3, the free energy of formation for this aluminosilicate phase was calculated to be -902.4 kcal/mole (25°C). Robie and Waldbaum (1968) report the standard free energy formation for kaolinite as -902.9 kcal/mole (25°). The agreement of these free energy values is certainly not conclusive proof that this aluminosilicate phase is kaolinite, but it does suggest that the phase is compositionally similar to kaolinite.

Figure 11 demonstrates that this system is not in equilibrium with respect to K^+- aluminosilicate phases. Although not shown here, the same is true for Na^+- aluminosilicate phases (Talbot 1977). The low abundance of K and Na compared to Al, Si, and Ca makes the interpretation of these elements difficult. The heterogeneous processes of K and Na are overshadowed by reactions involving more prevalent phases. However, the pH dependence of potassium and sodium is consistent with that exhibited by feldspar or mica-type phases (Figures 10g, 11, and 12). Figure 11 indicates that the solution proceeds toward equilibrium with either feldspar or mica-type phases. The reaction path followed by potassium indicates that equilibrium between a feldspar and mica phase would have been established with a logarithmic K^+/H^+ molar ratio of 7-8. The exact nature of these phases remains uncertain, since X-ray diffraction analysis did not reveal their composition.

Dominant heterogeneous processes involving aluminum and silica probably causes the K^+/H^+ ratio to decrease shortly after the leaching began (Figure 11). The movement of the K^+/H^+ ratio into the gibbsite stability field coincides with the apparent incongruent dissolution of the aluminosilicate phases described previously (Figures 7 and 10, a and b). Eventually the bulk solution begins to re-establish metastable equilibrium with the feldspar or mica-type phases. The attainment of metastable equilibrium is indicated by the increasing K^+/H^+ ratio, but the reaction rate and subsequent drop in pH are extremely slow owing to the apparent control by incongruent dissolution processes.

Iron--

Iron is also considered a major component of this hetergeneous system. Figure 13 shows the dissolved iron concentration as a function of the square root of leaching time. Iron may be present initially on the fly ash as complex oxides (Brimblecombe and Spedding 1975) and possibly as carbonates, sulfates, or carbides (for example, Fe_4C_3). These various iron compounds are rapidly dissolved, probably through hydrolysis reactions. Subsequently, iron precipitates since the solubility of hydrous ferric oxide is exceeded 2.6 times. The precipitation rate then decreases as $t^{1/2}$ increases. The slope of dissolved iron versus pH, plotted in Figure 10c, also indicates that hydrous ferric oxide exists over a wide pH range. X-ray diffraction patterns indicated that microcrystalline hematite was present, especially in the mid to high pH range.

A computer program was used to calculate the equilibrium constants

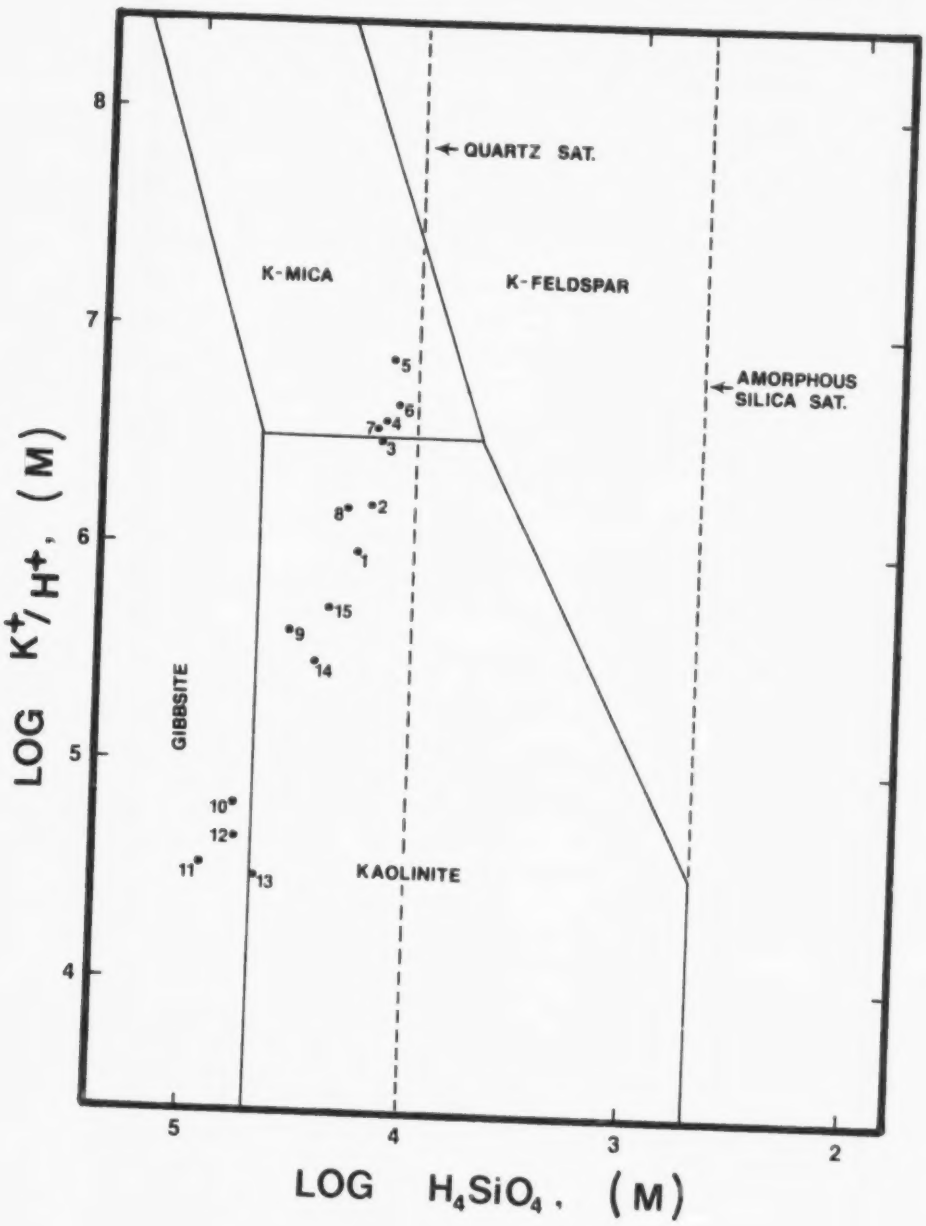


Figure 11. Silicate stability diagram with data points for K^+/H^+(wet delta ash) from the leaching experiments superimposed. Numbers are in consecutive order with respect to sampling intervals (short to long equilibration times) during the leaching experiments.

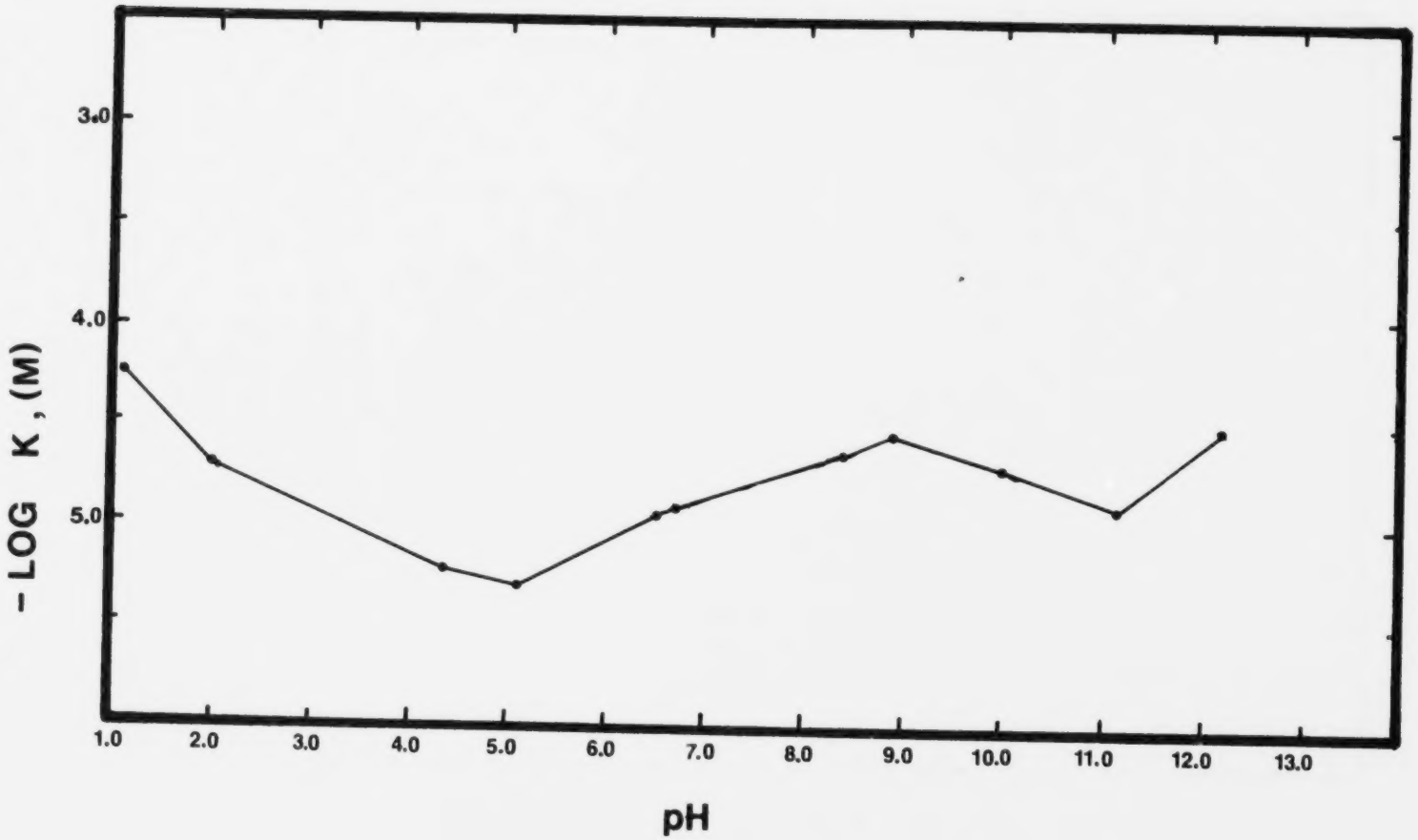


Figure 12. The change in dissolved potassium with pH as determined from experiments using ammonium hydroxide for pH adjustment.

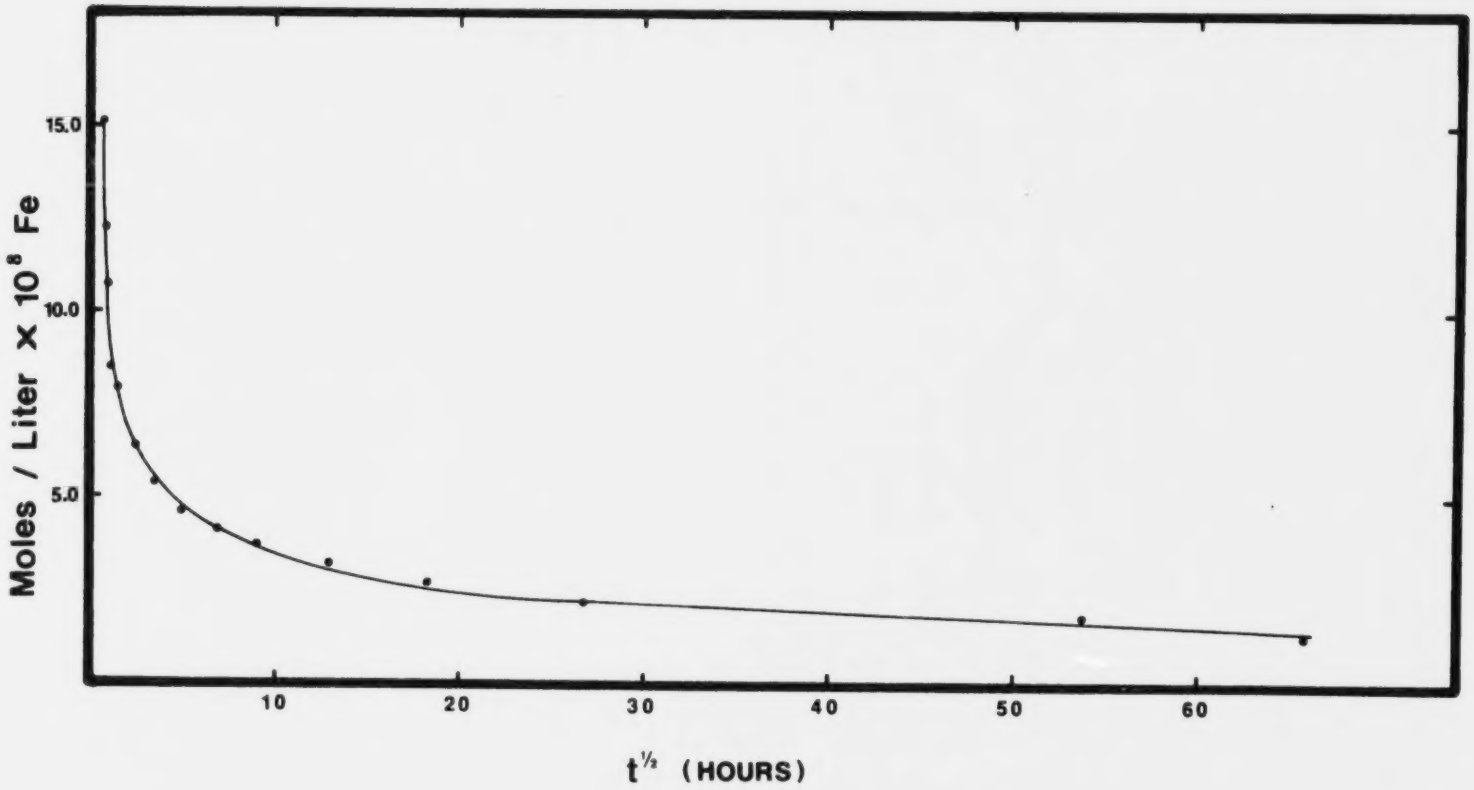


Figure 13. Dissolved iron as a function of the square root of leaching time.

corresponding to the hydrolytic reactions of hydrous ferric oxide with pertinent aqueous iron species. The program estimated the equilibrium constants (K_n) from a non-linear least-squares fit of experimental data points for dissolved iron versus pH. The calculated K_n values are presented in Table 11. They are referenced to 25°C and zero ironic strength ($\mu_{obs.}$ = 0.007). The free energy of formation ($\Delta G°$) for this hydrous ferric oxide

TABLE 11. EQUILIBRIUM CONSTANTS DESCRIBING FERRIC HYDROXIDE SOLID PHASE EQUILIBRIA WITH MAJOR AQUEOUS FERRIC COMPLEXES

Species	Log K_n[a]	Estimated log K_n[b]
$Fe(OH)_{3(s)}$	39.50	39.50
$Fe(OH)^{+2}$	13.30	13.37
$Fe(OH)_2^+$	22.70	22.70
$Fe(OH)_{3(aq)}$	31.00	32.66
$Fe(OH)_4^-$	33.50	34.56

[a]The reaction corresponding to K_n is $Fe^{+3} + nOH^- = Fe(OH)^{3-n}$.

[b]From Novozamsky et al. (1976).

phase was calculated to be -169.3 kcal/mole (25°C) from the estimated K_{SO} value. The standard free energy of formation for hydrous ferric oxide at 25° is -166.0 kcal/mole and for hematite -177.1 kcal/mole (Garrels and Christ 1965). Thus, the iron phase formed in this system appears to be partly microcrystalline in nature. At pH values above 3.0 the ferric oxide phase most likely controls the dissolved iron concentration.

Calcium and Magnesium--

The proposed relationships between calcium and magnesium in this system are shown in Figure 14. The distribution of the various phases was derived from basic equilibrium expressions listed in Table 12. The data points for calcium and magnesium fall directly on the phase boundary between calcite and dolomite. Hence, dissolved calcium and magnesium concentrations seem to be controlled exclusively by carbonate phases even at pH values where these solids are thermodyamically unstable.

At pH values greater than 10.5 magnesium precipitates, most likely as brucite (Figures 10d and 14). Consequently, calcium is released to the solution by the mixed carbonate phase due to mass balance constraints. The bulk solution then contains calcium in excess, and calcite (or argonite) apparently forms on the ash surface as described by Bricker and Garrels

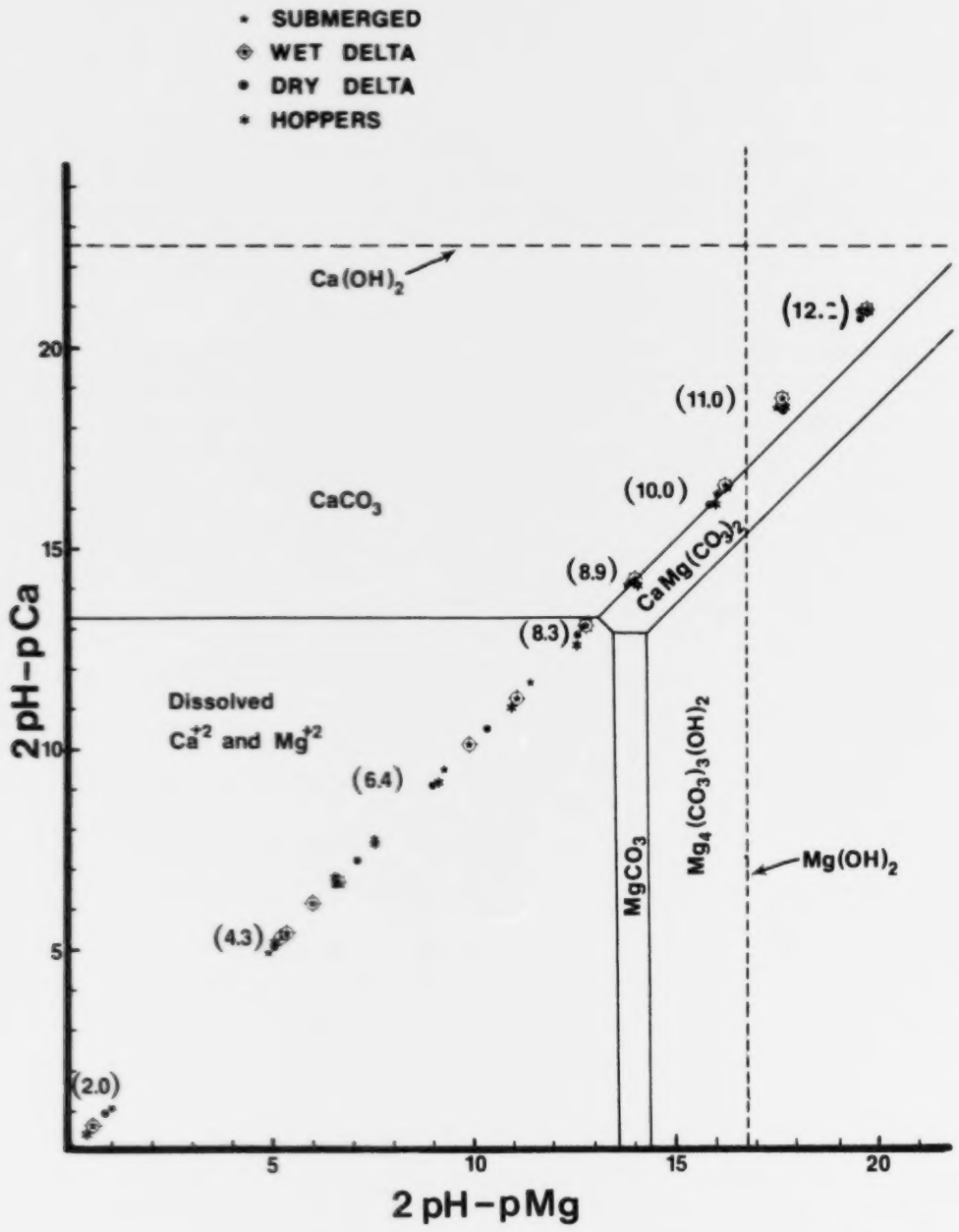


Figure 14. Solubilities of Ca^{+2} and Mg^{+2} carbonates and hydroxides at 25°C Numbers in parenthesis correspond to pH values observed during the electrophoretic mobility experiments

(1967). The presence of calcite at high pH was verified by X-ray diffraction analysis.

Phosphorous and Cadmium--

Phosphorus and cadmium were used to model the behavior of trace constituents typical of fly ash. Phosphorus was chosen owing to its importance in natural water eutrophication processes and cadmium because of its acute toxicity to aquatic organisms. Results of these experiments indicate that the trace element distribution between dissolved and

TABLE 12. LOG EQUILIBRIUM CONSTANTS AT 25°C AND LOG $_pCO_2$ = -3.52

Reaction	Log K	Source
$CaCo_3 = Ca^{+} + CO_3^{-2}$	- 8.35	Langmuir (1968)
$MgCO_3 = Mg^{+2} + CO_3^{-2}$	- 8.00	Garrels and Mackenzie (1967) Robie and Walbaum (1968)
$CaMg(CO_3)_2 = CA^{+2} + Mg^{+2} + 2CO_3^{-2}$	-16.70	Stumm and Morgan (1970)
$Mg_4(CO_3)_3(OH)_2 = 4Mg^{+2} + 3CO_3^{-2}\ 2OH^{-}$	-34.90	Garrels and Mackenzie (1967)
$Ca(OH)_2 = Ca^{+2} + 2OH^{-}$	- 5.43	Stumm and Morgan (1970)
$Mg(OH)_2 = Mg^{+2} + 2OH^{-}$	-11.15	Garrels and Mackenzie (1967)
$H_2O = H^{+} + OH^{-}$	-14.00	Schindler (1967)
$H_2O + CO_2 = HCO_3^{-} + H^{+}$	- 7.82	Schindler (1967)
$HCO_3^{-} = H^{+} + CO_3^{-2}$	-10.33	Schindler (1967)

particulate phases is strongly influenced by the major solid-phase components of this system. Adsorption and precipitation reactions appear to be controlling mechanisms in the appropriate pH regions.

The most important isoelectric point (pH_{IEP}) of the Columbia fly ash, with respect to natural water systems, occurs in the mid pH region near pH 7.55 (Figure 15). Essentially 100% of the aluminum and iron are associated with various phases on the ash particle in this pH region (Talbot et al. 1978). This suggests that the surface characteristics of the ash are controlled by these incipient phases (e.g., $Al(OH)_3$ and $Fe(OH)_3$). Figure 10h demonstrates that almost all phosphorus (99.8%) is removed from solution as the pH decreases from 8.5 to 4.0. Huang (1975) observed a similar pH dependence for phosphorus adsorption on amorphous aluminum hydroxide. The

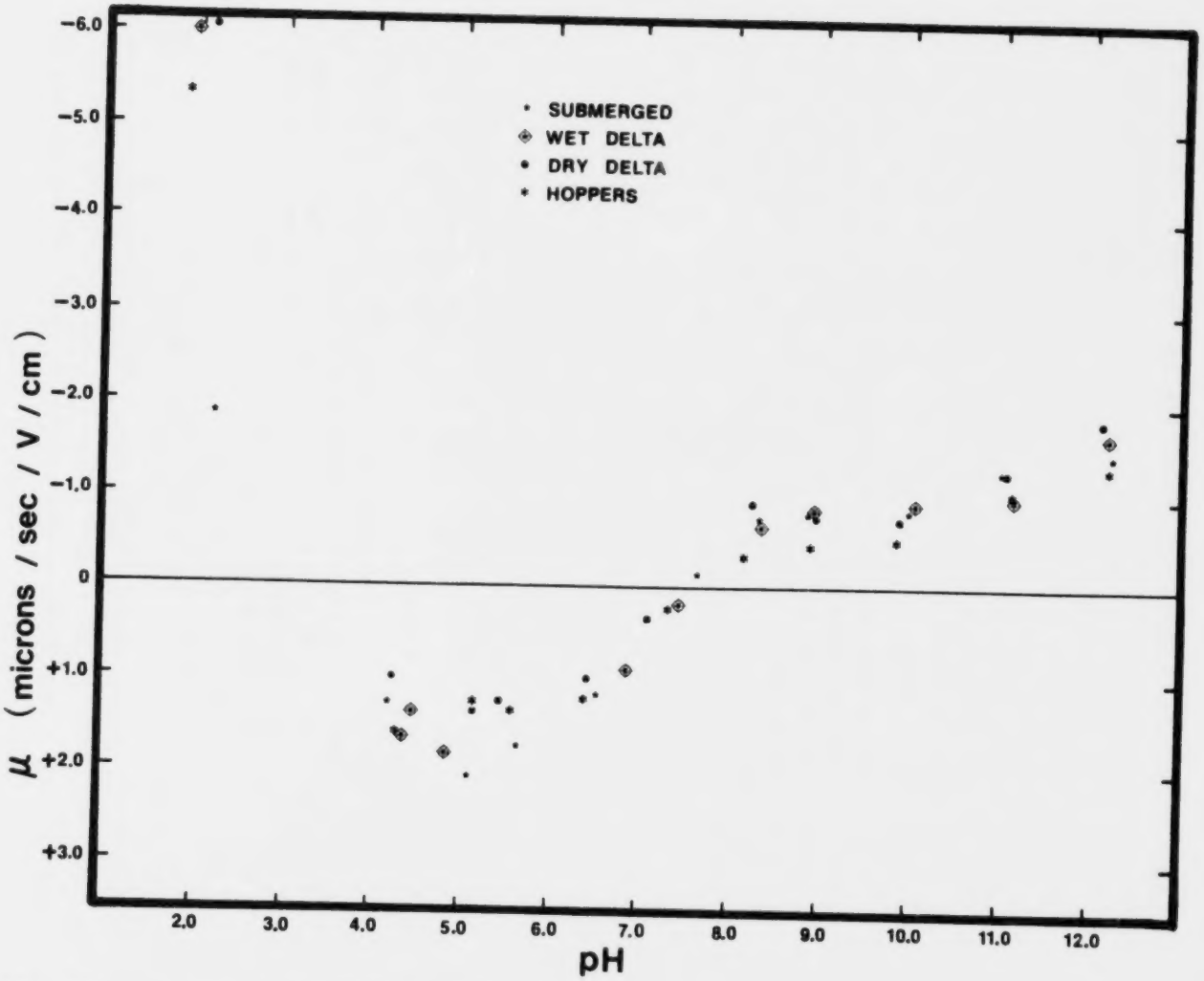


Figure 15. Electrophoretic mobilities of Columbia fly ash suspensions as a function of pH.

reason for the slight variation in dissolved cadmium concentrations in the same pH region may be caused by the heterogeneus nature of the fly ash.

The appearance of both cadmium and phosphorus in the bulk solution at low pH results from ash particle dissolution. Only 5% of the phosphorus remains on the ash particle at pH 1.0. In contrast, approximately 90% of the cadmium is still associated with the ash particle. Cadmium is apparently strongly adsorbed to the ash surface at low pH values. Trace anions, however, seem to be almost entirely released to the dissolved phase. Hence, adsorption reactions appear to completely control the dissolved trace element concentrations at low pH. Further investigation of the release of potentially toxic anions such as arsenic and boron is probably warranted.

At the high pH values observed in the ash pond (Andren et al. 1976, 1977) calcium and magnesium carbonate and hydroxide phases may control the surface characteristics of the fly ash. In addition, hydrous ferric oxide may also partly determine the identy of the ash surface at elevated pH values. The carbonate phases of calcium and magnesium do not have large adsorption capacities or strengths for trace metals (Parekh et al. 1977). Nevertheless, the respective carbonate and hydroxide solubilities of the trace metals should keep their dissolved concentrations low. For instance, at pH 11.0 the cadmium concentration is about 10^{-9} . Since $K_{sp} = (Cd^{+2})(OH^{-})^2$, we have $(10^{-9})(10^{-3})^2 = 10^{-15}$. The reported K_{sp} for $Cd(OH)_2$ is $4x10^{-15}$ (Stumm and Morgan 1970). Similarly, assuming CO_2 saturated conditions, K_{sp} for $CdCO_3$ is $5x10^{-12}$. These calculations suggest that the carbonate and hydroxide phases are controlling mechanisms for dissolved cadmium at high pH. The same is probably true for other chemically similar transition metals.

The simultaneous decrease of dissolved calcium and phosphorus at pH 10.0 (Figures 10, e and h) implies that phosphorus precipitates as a hydroxyapatite-type phase or is removed by occlusion via co-precipitating magnesium calcites. Using hydroxyapatite as an example, we can calculate the corresponding ion activity product according to the reaction:

$$5\ Ca^{+2} + 3PO_4^{-3} + OH^{-} = Ca_5(PO_4)_3\ OH_{(s)} \qquad (6)$$

Then, $K_{sp} - (Ca^{+2})^5\ (OH^{-})\ (PO_4^{-3})^3$ where $K_{sp} = 10^{-55.6}$ (Stumm and Morgan 1970). Substituting values obtained from plots of dissolved concentration and estimating the dissolved PO_4^{-3} concentration by:

$$[PO_4^{-3}] = \frac{7.8x10^{-13}[HPO_4^{=}]}{[H^{+}]}$$

the concentration of PO_4^{-3} is 1.2×10^{-8} . The ion product for hydroxyapatite can be computed by:

$$(10^{-3.6})^5 (10^{-3}) (10^{-7.9})^3 = 10^{-45} \text{ at pH 11} .$$

This apparent oversaturation may reflect the influence of the chemical composition of the aqueous phase (Corsaro and Sutherland 1967), kinetic factors (Jenkins et al. 1971), and hindrance by magnesium on nucleation and growth (Berner 1975). Although specific adsorption of phosphorus can substantially decrease its dissolved concentration (Malotky 1978), it appears to have minimal influence here. Further investigation of the controls on the trace element distribution is needed before a rigorous explanation of these processes can be attempted.

MONITORING STUDY OF THE COLUMBIA ASH BASIN

In addition to the laboratory leaching experiments, a monitoring study of the ash basin at the Columbia Generating Station was conducted from June 1976 to April 1977. The study had two objectives: (1) To identify potential environmental hazards associated with fly ash leachates and to compare these to the results of the laboratory studies, and (2) to characterize the surfaces of suspended sediments in different parts of the ash basin.

The ash basin is normally well mixed with regard to chemical and thermal stratification. Except for ice cover during the winter of 1976-77, surface and bottom water samples exhibited nearly identical chemical compositions.

Variations in dissolved elemental concentrations typically demonstrated horizontal gradients (from the first ash basin to the second) when the plant was operational. Dissolved chemical concentrations were a function of flow rate and therefore presumably were controlled by kinetic constraints since many of the elements were often supersaturated.

Figures 16 and 17 summarize the data obtained for the monitoring period for average major element concentrations in the ash basins and source water (the cooling pond and the Wisconsin River). High pH values are associated with this fly ash leachate (see previous discussion). Extremely high pH values (>12) occurred after December 1976 when Na_2CO_3 was added to the fly ash to improve the efficiency of the electrostatic precipitators. Average concentrations of silica and alkalinity were also greater in the ash basins than in the source waters. Their concentration trends behave similarly to pH after the addition of Na_2CO_3 commenced. In the case of silica one would expect greater solubility of silicic acid in the pH ranges present in the ash basin.

Phosphorus concentrations in the ash basin were normally less than the

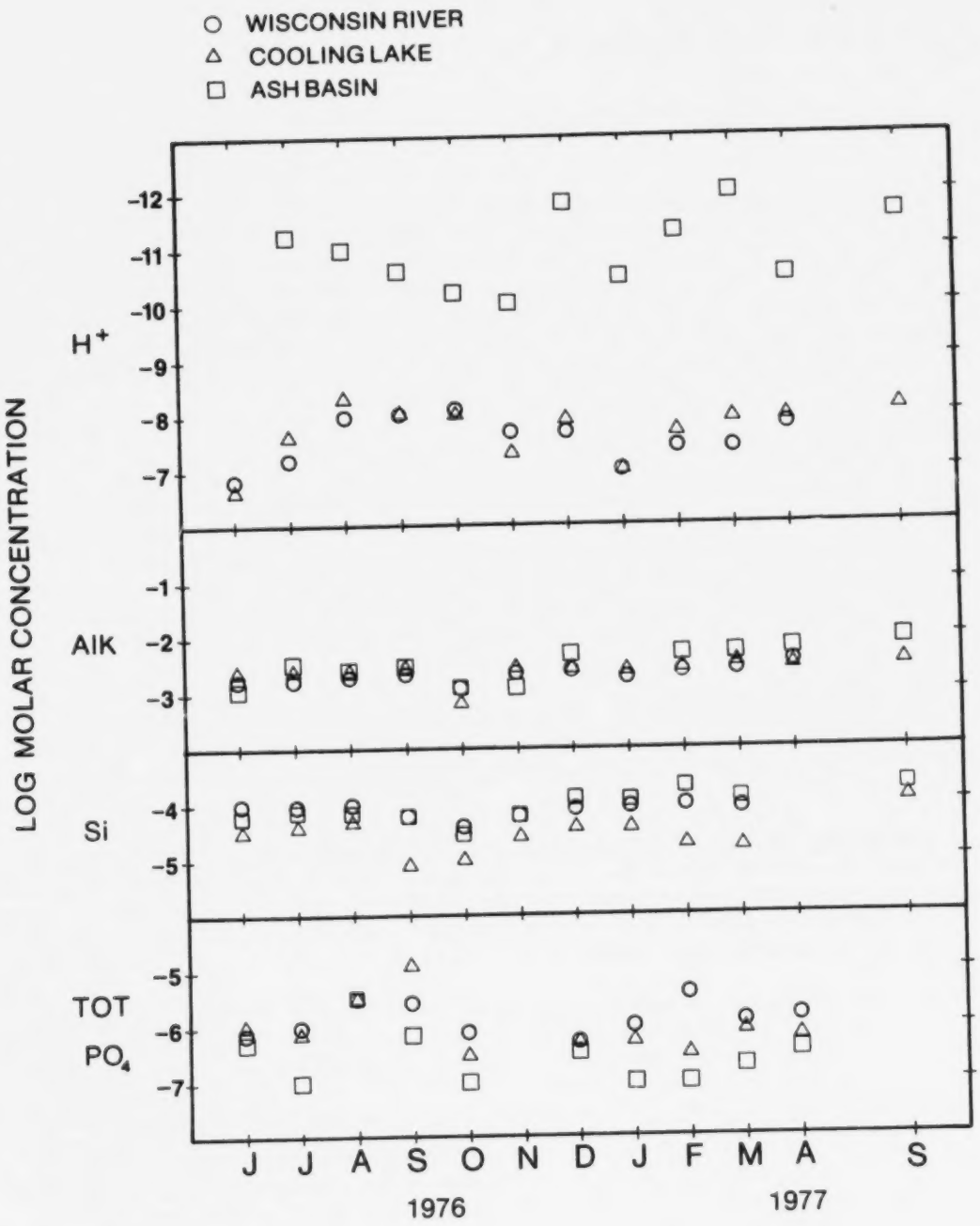


Figure 16. Monthly comparison of Wisconsin River, cooling lake, and ash basin analyses.

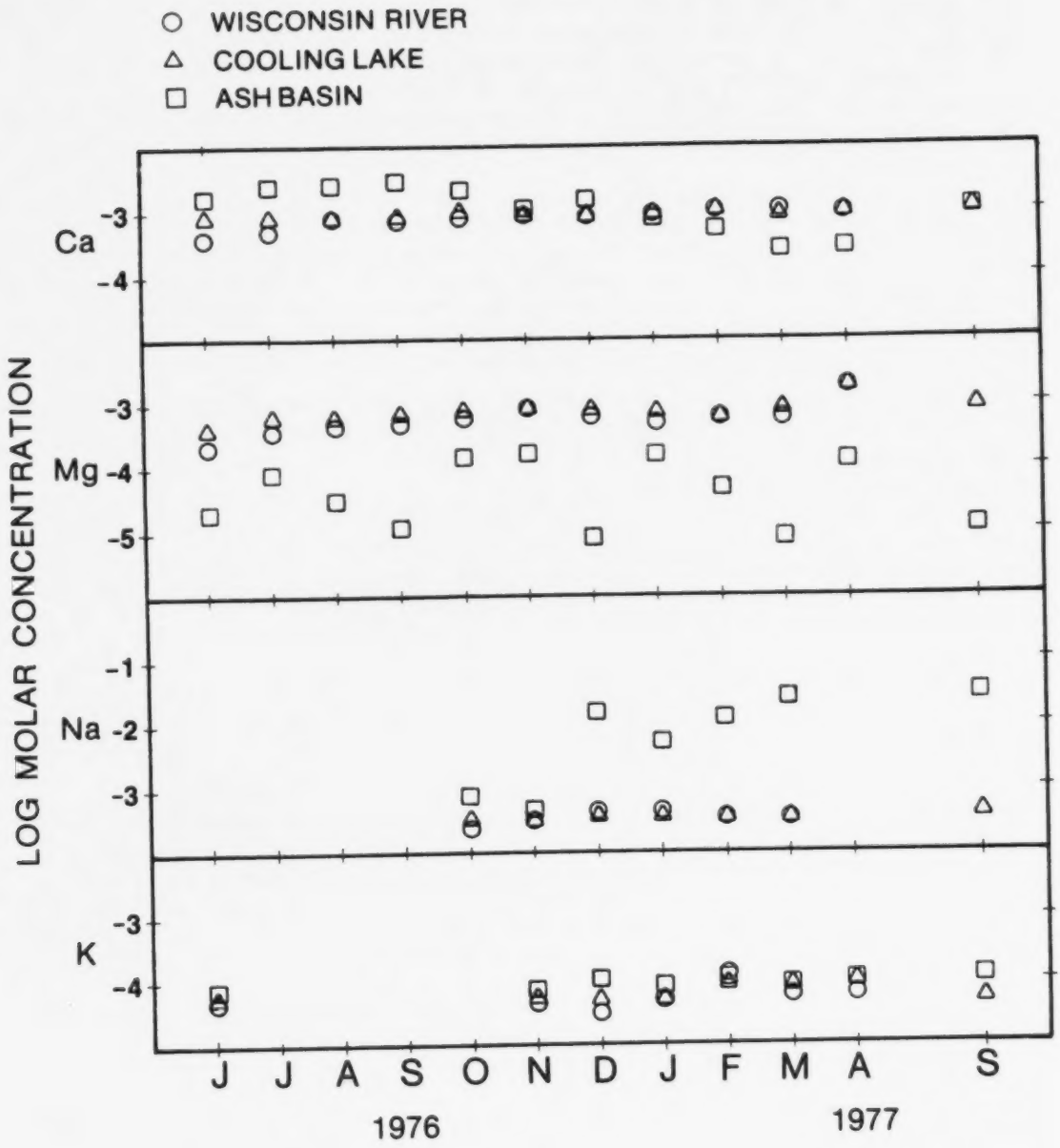


Figure 17. Comparison of average Na, K, Mg, and Ca concentrations in the Wisconsin River, cooling lake, and ash basin.

concentrations found in the cooling pond. This indicates that phosphorus (and organic matter) is being adsorbed on the fly ash particles deposited on the ash delta. On several occasions anomalously high values were observed. However, these high phosphorous values were usually associated with abnormal turbidity during periods of high wind action. Previous studies (Tenney and Schelberger 1970, Higgins et al. 1976) have demonstrated the adsorptive properties of fly ash.

Figure 17 illustrates the concentrations of sodium, potassium, calcium, and magnesium in the ash basins and cooling pond at the Columbia station. Elevated sodium and potassium concentrations are expected since hydrolyses of their respective oxides are attributed to be one of the reactions leading to an elevated pH (see previous section). The sodium concentrations reach exceptionally high concentrations in December, again resulting from the addition of Na_2CO_3. Concentrations of magnesium are usually below those observed in the source waters. Previous calculations have demonstrated that the solubility product of brucite ($Mg(OH)_2$) is exceeded and the data suggest that the element is retained in the ash delta as the water percolates through the deposited fly ash. The profile after December 1976 is completely opposite to the pH trends observed in Figure 16. The behavior displayed by calcium demonstrates that average levels of dissolved calcium were much higher than the source water prior to December 1976 and that after this period calcium was also precipitating and being retained in the fly ash delta.

Figure 18 illustrates average iron, aluminum, copper, and chromium concentrations in the ash basins. Iron is normally near the detection limit although high values are observed in March and April 1977. These high values can possibly be explained as an artifact of filtration since colloidal iron may pass through a 0.4-μm filter. Ash basin aluminum concentrations exceeded source water concentrations by a magnitude of 100 to 1,000 at all times during the study. This is consistent with the laboratory experiments. The concentrations of copper and chromium demonstrate that both elements are liberated after interaction of cooling pond water with fly ash. The elevated copper concentrations are not consistent with laboratory equilibrium experiments and may be due to kinetic factors.

Table 13 demonstrates the results obtained from the MINEQL computer program for calculating thermodynamic equilibrium concentrations. Only species present at greater than 1% of the total concentration are reported. For these calculations the pH was held at 11.5 and redox reactions were not considered. Many of the elements are predicted to remain in solution as soluble complexes; several of the cations have soluble hydroxy complexes (Al, Fe, Cr, Cd, and Pb) and presumably would exist in solution as anionic species. The computer results suggest that silica would not precipitate. However, soluble silica decreases in the ash basin when pumping is interrupted, and zeolites (aluminosilicates) have been identified in the ash delta. (Helmke et al. 1977). Solid phases predicted by the program include $CaCO_3$, $Al(OH)_3$, $Mg(OH)_2$, $Fe(OH)_3$, $Cu(OH)_2$, $Ba\ SO_4$, and $Pb(OH)_2$. (Several of these solid phases were identified in the previously

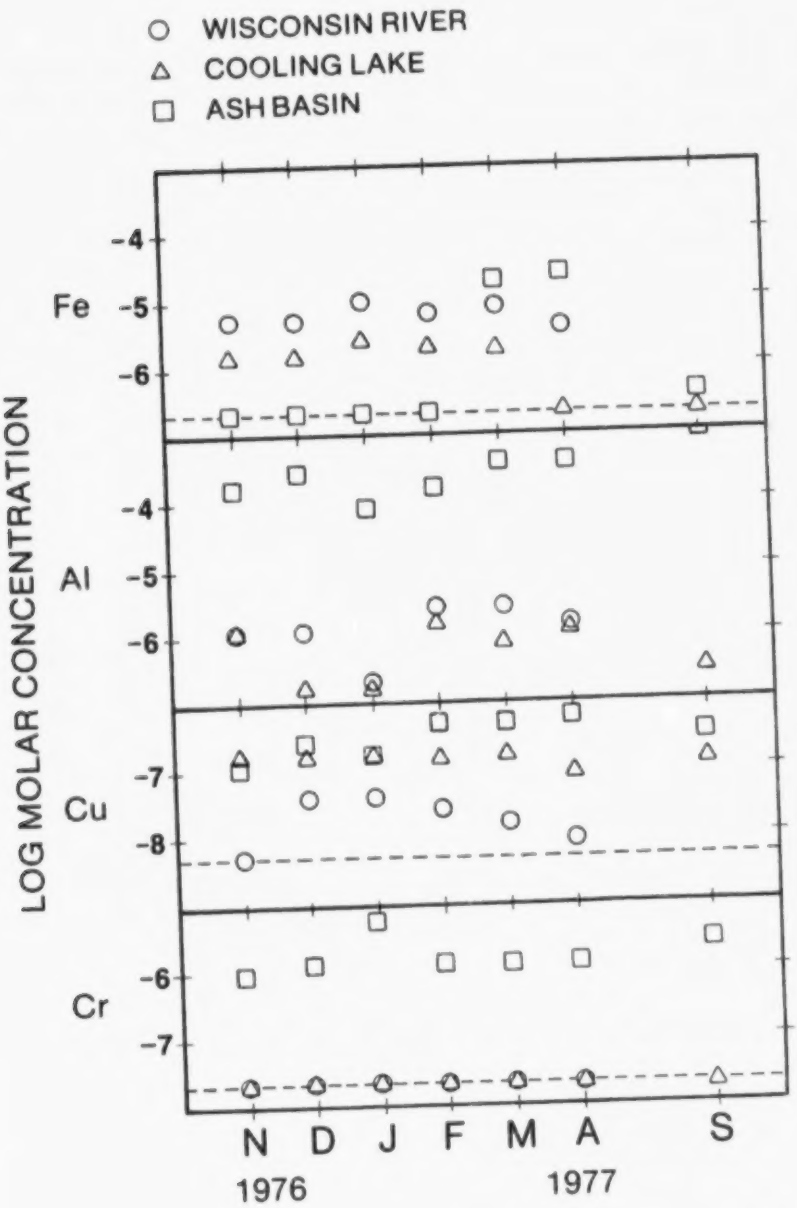


Figure 18. Comparison of cooling lake and Wisconsin River dissolved metal concentrations with those observed in the ash basin.

TABLE 13. MINEQL COMPUTER PROGRAM RESULTS FOR SOLUBLE CONCENTRATIONS OBSERVED DURING THE SEPTEMBER 1977 SAMPLING PERIOD (25°C)

Element	Initial concentration[a]	Soluble species	%	Precipitate	%
CO_3	2.6×10^{-3}	$CO_3^{=}$	36	$CaCO_3$	51
		$NaCO_3^-$	12		
		HCO_3^-	1		
Cl	4.2×10^{-4}	Cl^-	100		
H_4SiO_4	1.5×10^{-4}	$H_3SiO_4^-$	96		
		$H_2SiO_4^{=}$	3		
		H_4SiO_4	1		
Al	1.1×10^{-4}	$Al(OH)_4^-$	7	$Al(OH)_3$	93
SO_4	1.2×10^{-2}	$SO_4^{=}$	90		
		$NaSO_4^-$	10		
Na	3.1×10^{-2}	Na^+	95		
		$NaSO_4^-$	4		
		$NaCO_3^-$	1		
Ca	1.3×10^{-3}			$CaCO_3$	98
Mg	3.0×10^{-5}	$MgAl(OH)_4^+$	2	$Mg(OH)_2$	95
		$MgSO_4$	1		
K	1.1×10^{-4}	K^+	91		
		KSO_4^-	9		
Fe	8.0×10^{-7}	$Fe(OH)_4^-$	26	$Fe(OH)_3$	74
Cu	3.8×10^{-7}			$Cu(OH)_2$	100

(continued)

TABLE 13 (continued)

Element	Initial concentration[a]	Soluble species	%	Precipitate	%
Ba	4.4×10^{-6}			$BaSO_4$	100
H_4BO_4	4.0×10^{-4}	H_4BO_4	100		
Cr	1.9×10^{-6}	$Cr(OH)_4^-$		100	
Cd	2.5×10^{-8}	$Cd(OH)_3^-$	64		
		$Cd(OH)_2$	34		
		$Cd(OH)^+$	1		
Pb	4.8×10^{-9}	$Pb(OH)_3^-$	61	$Pb(OH)_2$	29
		$Pb(OH)_2$	10		

discussed laboratory solubility studies.)

The limitations of this computer model are based primarily on the completeness of the number of reactions and the accuracy of the formation constants. Additionally, the model implies thermodynamic equilibrium, a condition obviously not found in the ash basins. However, the model is useful for predicting possible solid phases and represents a first attempt at understanding the chemistry of the system. As stated previously, kinetic constraints cannot be handled and adsorption reactions are not included in the calculations.

Table 14 compares the range of potentially toxic elemental concentraions observed in the ash basin with literature values for water quality criteria. With the exceptions of lead and arsenic, all the elements listed in the table could have a deleterious effect on the quality of receiving waters. Aquatic life is normally absent in the ash basin, and these concentrations, in conjunction with the extremely high pH values recorded in the basin, may provide one explanation for this observation.

TABLE 14. COMPARISON OF SUGGESTED WATER QUALITY CRITERIA WITH VALUES OBSERVED IN THE ASH BASIN

Element	Concentrations possibly toxic to aquatic life (mg/liter)	Range observed in ash basin (mg/liter)
Al	1.0[a]	0.02 - 52.6
As	0.5[b]	0.006 - 0.216
B	0.22[b]	0.1 - 6.4
Cd	0.0001[b]	0.0001- 0.004
Cr	0.1[b]	0.066 - 0.142
Cu	0.01[b]	0.010 - 0.028
Pb	0.030[b]	<0.002
Zn	0.030[b]	<0.01 - 0.04

[a]Resources Agency of California (1960).
[b]Van Hook and Shutts (1976).

Figures 19 and 20 indicate that the rate of aluminum and chromium precipitation is enhanced between the ash basin and the discharge water. This enhancement results from the present practice at the Columbia Generating Station of neutralizing the ash basin effluent with sulfuric acid. Despite partial removal of some elements (Al and Cr), concentrations are sufficiently high to be viewed as potentially toxic in receiving waters composed of a significant fraction of ashpit discharge. It may be advantageous, using current facilities, to neutralize ash basin effluent

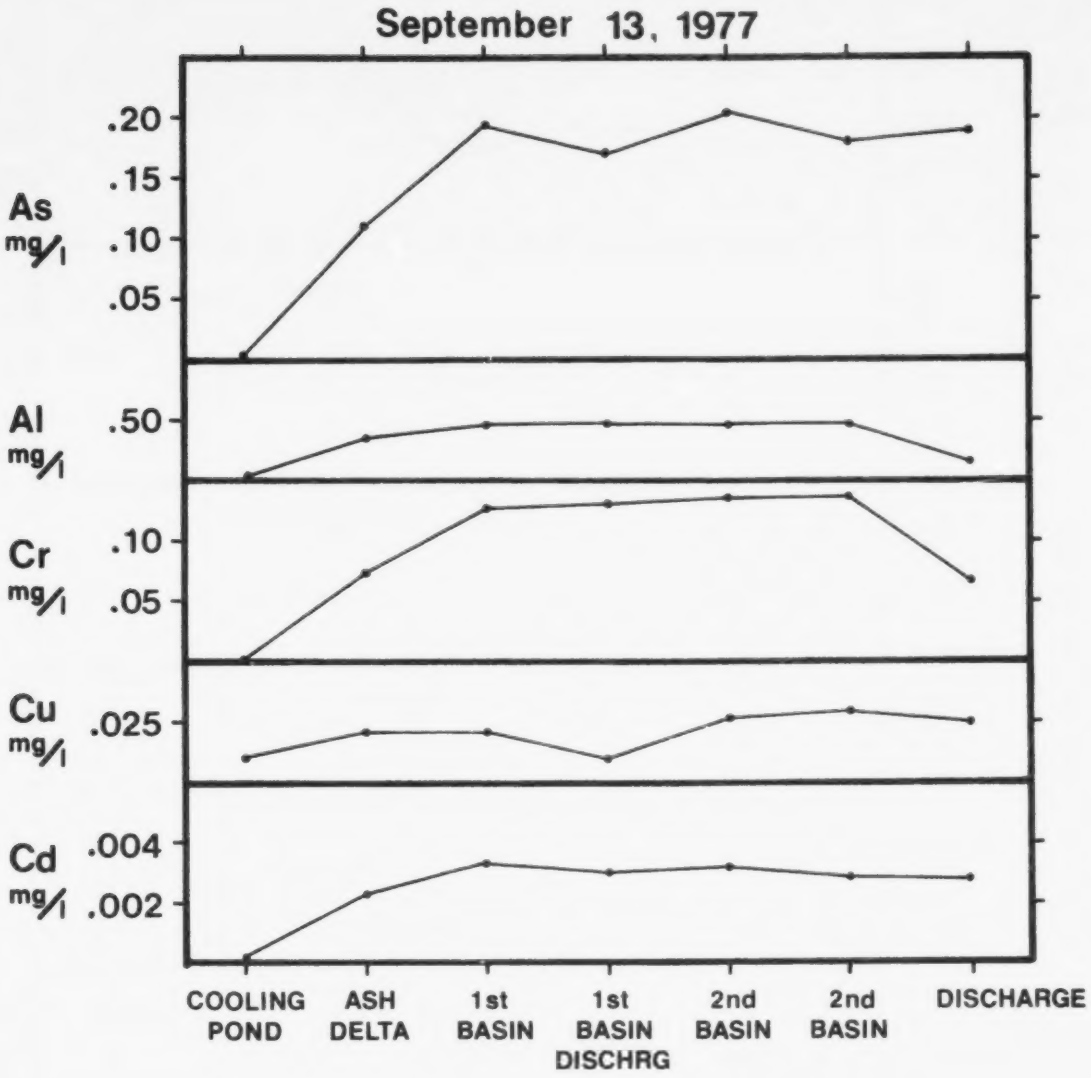


Figure 19. Soluble element concentrations at various stations at the Columbia plant for September 13, 1977.

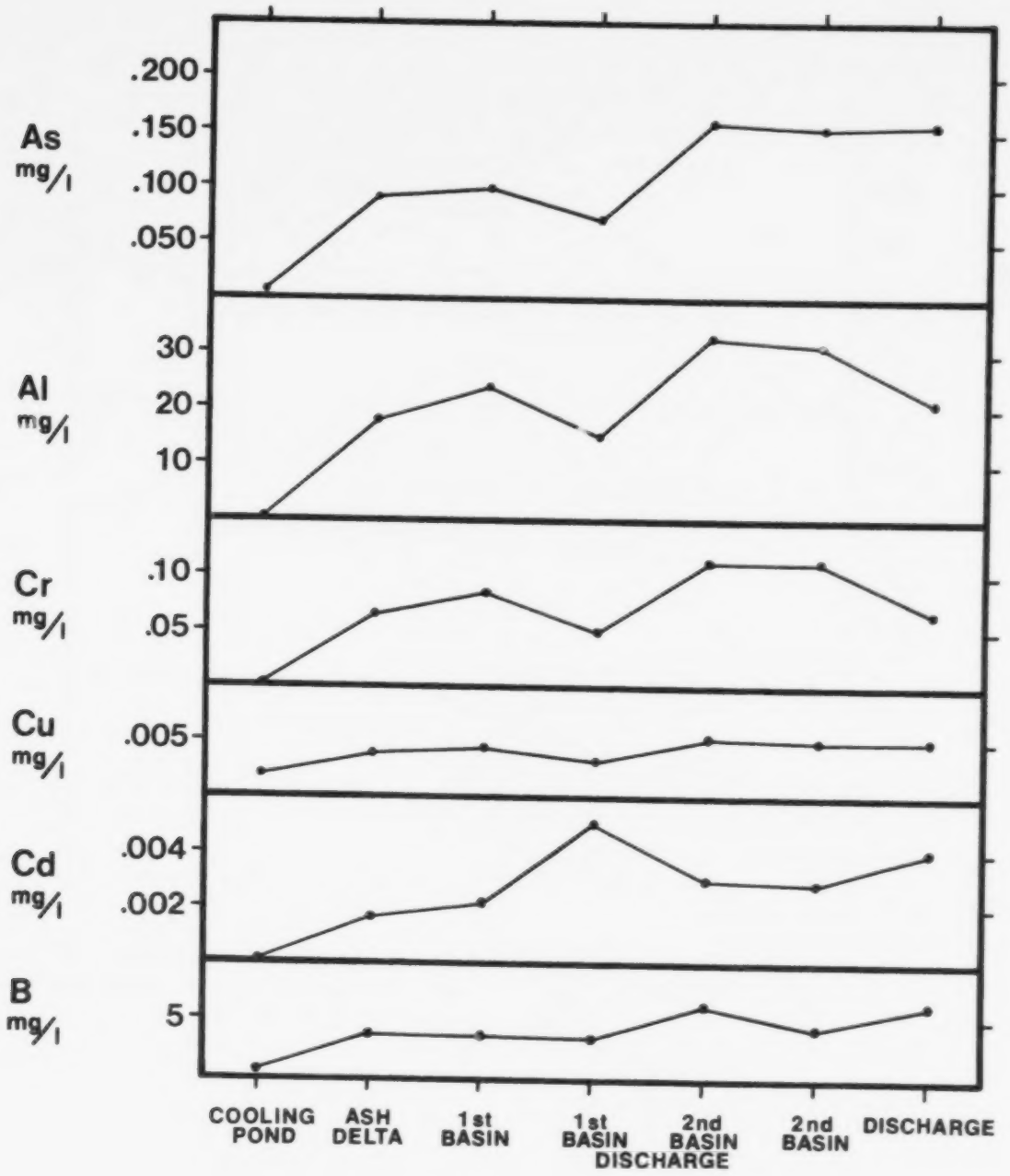


Figure 20. Soluble element concentrations at various stations at the Columbia plant for September 27, 1977.

prior to the final settling basin. This process may facilitate sedimentation of flocculated aluminum with subsequent partial removal of several additional toxic elements.

The second objective of the study of the Columbia ash basin was to characterize the surfaces of the sediments in the ash basins. Suspended sediments, collected in sediment traps during the September 1977 sampling period, were examined by scanning electron microscopy (SEM) and X-ray diffraction.

Figure 21 is a (SEM) picture of fly ash particles blown on shore in the second fly ash basin. The characteristically spherical fly ash particles serve as a nucleus for precipitation reactions in the basin. Figure 22 represents a picture of precipitate removed from the float of a sediment trap in the second basin. X-ray emission and X-ray diffraction analyses of this sample suggest that it is composed primarily of calcite. The crystal structure is not the normal cubical crystal observed for this mineral phase; instead this crystal has a structure similar to calcite containing trace quantities of magnesium (Berner 1975).

X-ray diffraction analyses were made of sediment samples obtained in the first and second ash basins and of the windblown precipitate and float precipitate pictured in Figures 21 and 22. Qualitative surface X-ray emission analyses of all samples demonstrated the presence of Al, Si, S, K, Ca, Mg, Ba, and Fe in varying degrees. However, Ca usually predominated (particularly in the sediment float sample).

Figure 23 illustrates the diffraction peaks observed in the windblown precipitate. Calcite ($CaCO_3$), quartz (SiO_2), and gypsum ($CaSO_4.2H_2O$) peaks can be readily observed. Barite ($BaSO_4$), magnetite (Fe_3O_4), apatite ($Ca_5(PO_4)_3(F,Cl,OH)$), and potassium chabazite ($CaAl_2Si_4O_{12}.6H_2O$) may also be present although overlapping peaks tend to obscure the relative X-ray intensities characteristic of the respective minerals. Additional peaks have not been identified at this time.

Figure 24 depicts the X-ray diffraction peaks observed in the precipitate that was scraped off the walls of the sediment trap float positioned in the second ash basin. Evidence for the presence of calcite ($CaCO_3$) and magnetite (Fe_3O_4) is apparent although peaks for the other mineral phases discerned in Figure 23 were not observed. Of particular significance is the absence of the quartz peaks present in all the other diffraction analyses. This suggests that quartz in the sediments can be attributed to resuspended shore material or that quartz was originally present in the discharged fly ash. Many of the peaks present in this figure have not been identified.

Figures 25 through 28 display the results obtained from X-ray diffraction analyses of suspended sediments collected by traps in the first basin (near the ash delta) and the second basin of the ash pond. The figures indicate that the sediments become more complex (with additional

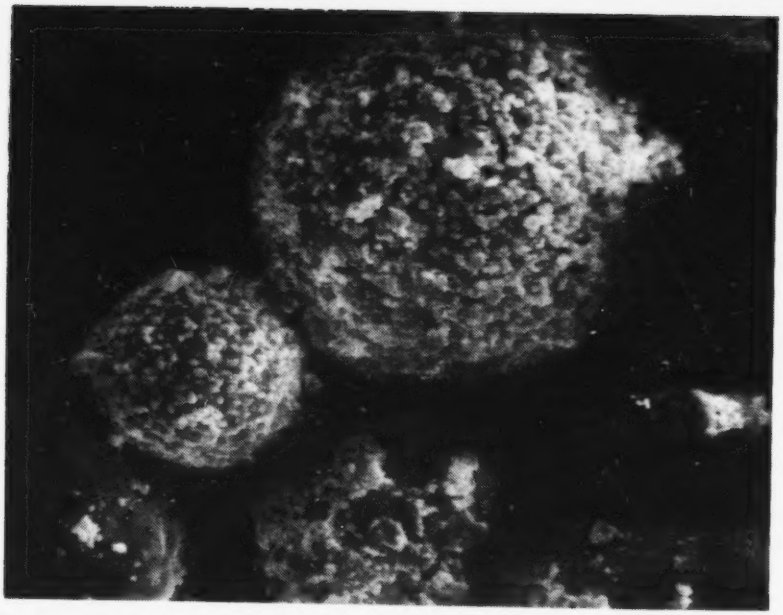


Figure 21. Scanning electron microscope picture of windblown precipitate from the shore at the second basin of the Columbia ashipt (magnification = 100).

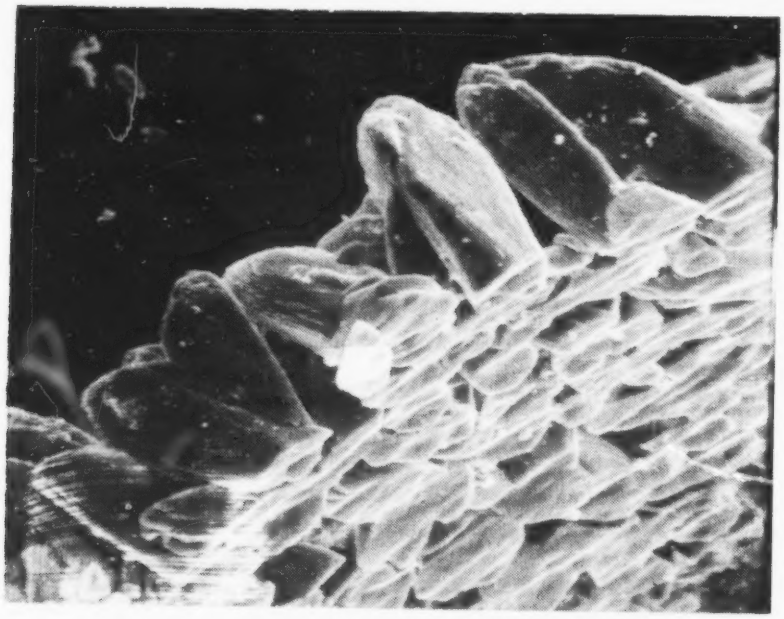


Figure 22. Scanning electron microscope picture of the precipitate formed on the sediment trap float in the second basin of the Columbia ashpit (magnification = 100).

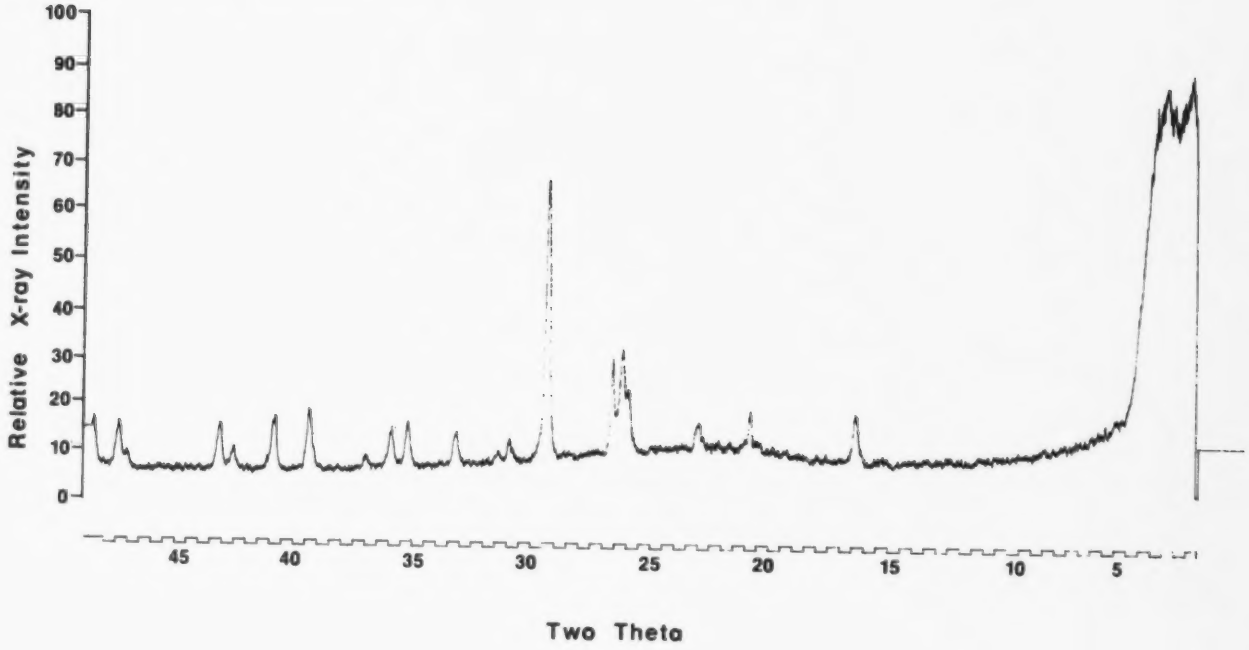


Figure 23. X-ray diffraction pattern for windblown precipitate in the second basin.

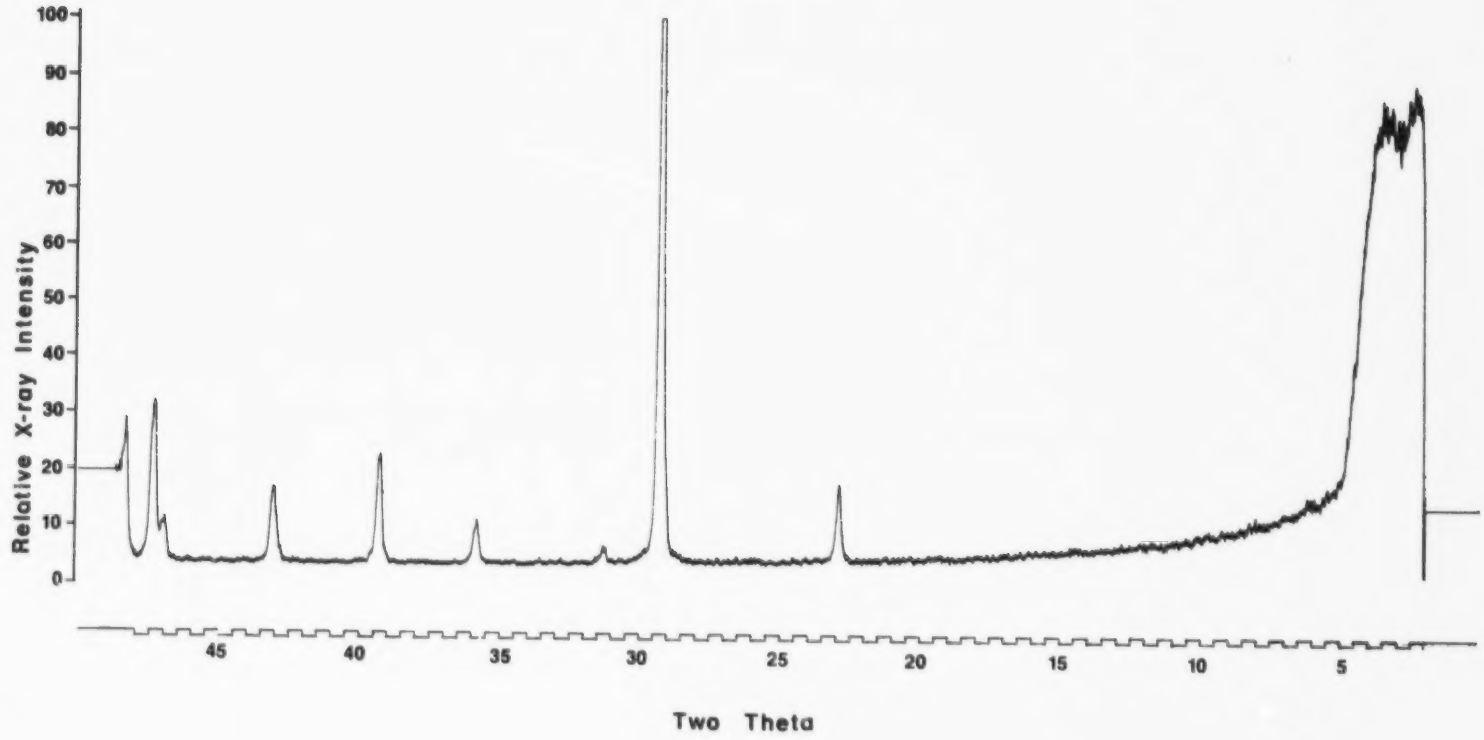


Figure 24. X-ray diffraction pattern for precipitates on a float in the second basin.

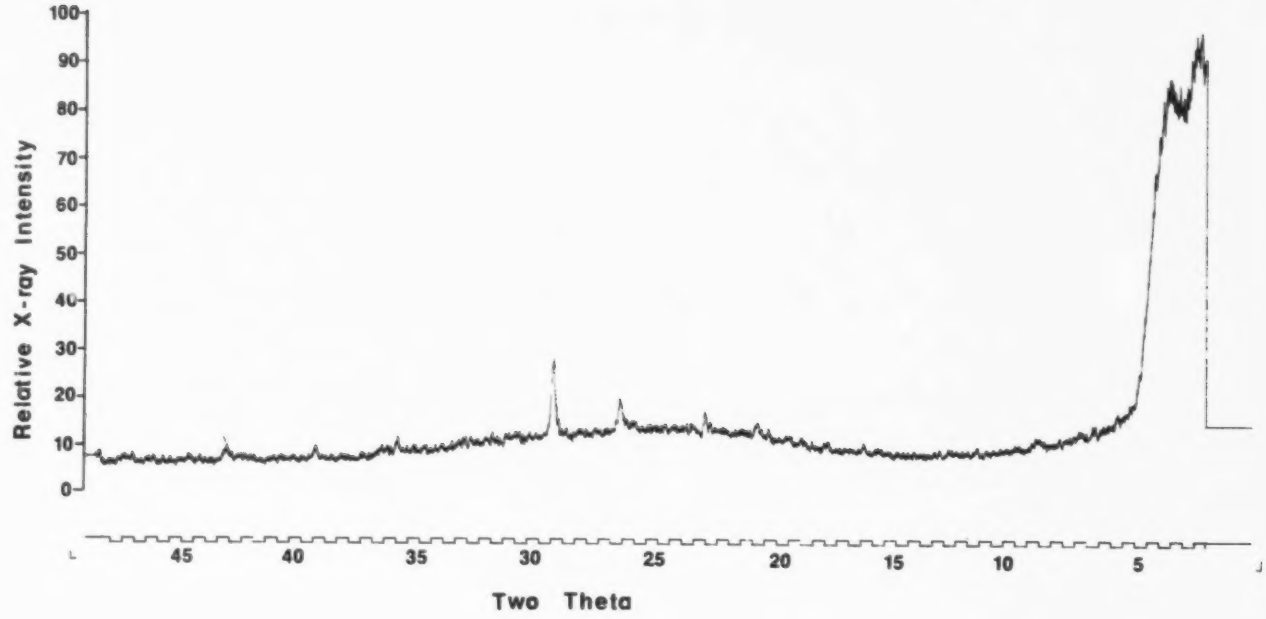


Figure 25. X-ray diffraction pattern for surface-suspended sediments in the first basin.

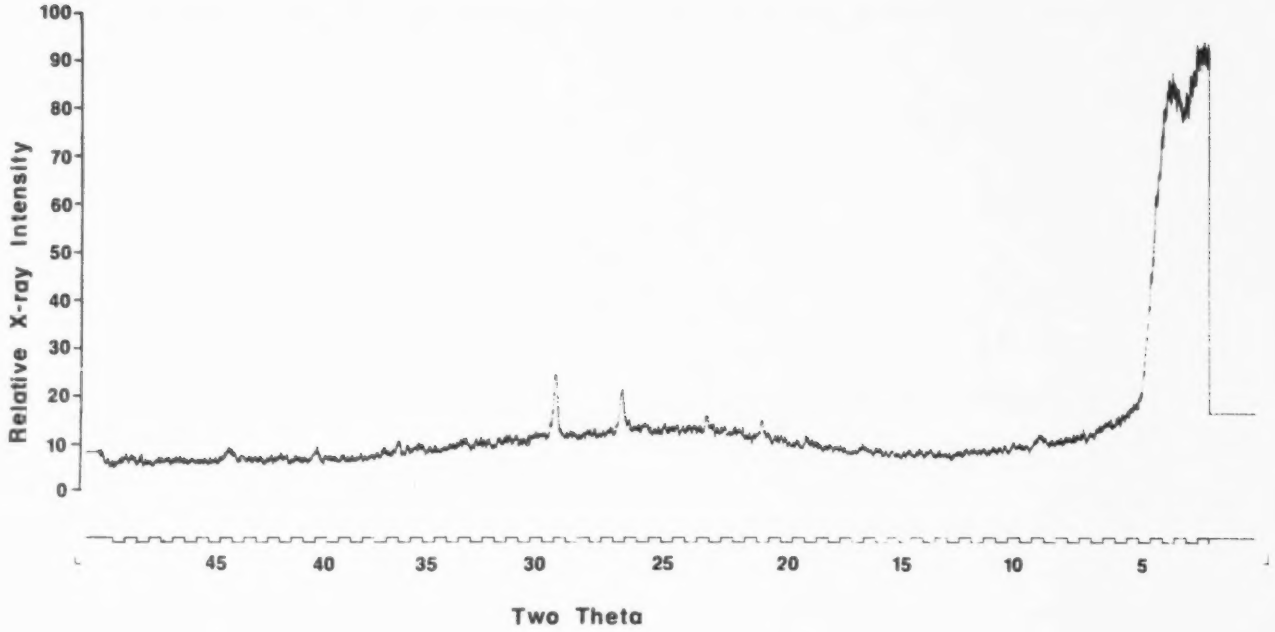


Figure 26. X-ray diffraction pattern for sediments from the first basin.

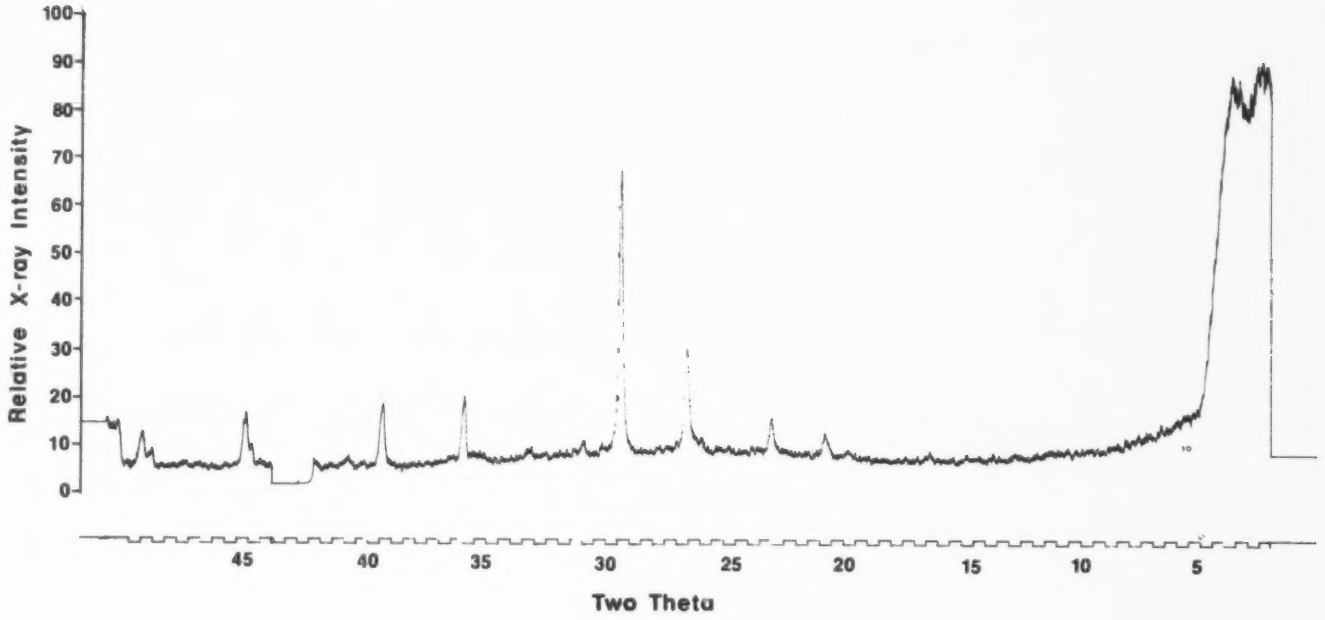


Figure 27. X-ray diffraction pattern for sediments from the first station in the second basin.

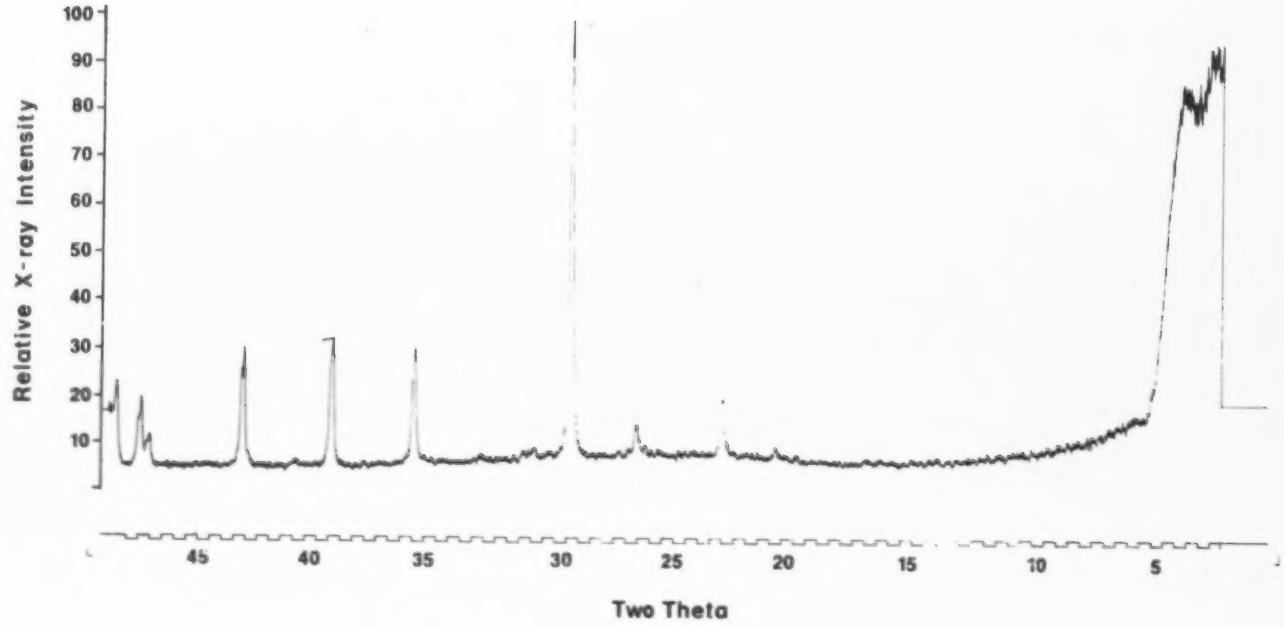


Figure 28. X-ray diffraction pattern for sediments from the second basin.

mineral phases) and increasingly crystalline with distance from the initial deposition site. Both patterns demonstrate the presence of quartz, gypsum, and calcite although a magnetite peak is absent from the analyses of sediment from the first basin. Additional peaks remain to be identified.

Groundwater Contamination From The Ash Basin

Contamination of groundwater by fly ash leachate has been documented by Theis and Richter (1978). The authors presented evidence which suggested that equilibrium groundwater concentrations could be partially predicted utilizing current adsorption models. This model was run for elemental concentrations in the presence of various metal oxides of a relatively well-characterized soil. However, the present literature dealing with the movement of contaminants through various soild systems suggests that several mechanisms (that is, other than adsorption) may be responsible for controlling elemental mobilities in groundwater. Korte et al. (1975) demonstrated that the mobility of several transition metals is highly dependent on the chemical form of the element and the iron and manganese content of the soil. Thus, some elements may be partitioned by adsoprtion on the various soil components (that is, organics, clays, or hydrous oxides), and other elements may precipitate. Regardless of whether adsorption or precipitation constitutes the primary removal mechanism, one may predict that a given soil volume eventually becomes saturated (given a constant input). The movement of chemicals through groundwater systems can thus be viewed as a natural chromatographic process with the more conserative elements traveling faster than transition metals. This phenomenon could be exploited to diagnose whether groundwater contamination will be a problem. That is, if elements such as Na, Cl, or SO_4 do not appear in the vicinity of fly ash disposals, the more toxic elements such as Pb, Cd, Zn, and Cu would also be immobilized.

Groundwater infiltration at the Columbia ash basin is not well understood. Some ash basin water percolates into the lower soil profile (Anderson and Andrews 1976). There is also evidence, however, that ash basin water infiltrates directly through the dikes and remains perched on the surface of the adjacent sedge meadow. This infiltration may provide one explanation for the difficulty in providing conclusive evidence of ash basin contamination in water samples taken from wells placed at incremental distances from the ash basin. Some of the wells may intersect contaminated sub-surface water flows while others may not.

Some evidence, however, suggests that ash basin leachate is influencing the water quality of the surrounding groundwater. For example, well-water samples obtained prior to plant operation (April 1975) demonstrated boron concentrations of less than 0.09 mg/liter. Subsequent analysis of samples demonstrated concentrations ranging from <0.09 mg/liter to 0.82 mg/liter (analysis performed by Swanson Environmental, Inc.). Analysis of our well-water samples obtained in September 1977 (Table 15) suggested boron concentrations of approximately 0.3 mg/liter. Boron may be present in the ash basin at concentrations in excess of 5 mg/liter (Table 14) and is considered relatively inert with regard to precipitation reactions (Hem

1971). In addition, the current literature suggests that the element is relatively mobile in the soil column (Braustein et al. 1977). Thus boron contamination of groundwater is apparently occurring around the ash basin at the Columbia Generation Station. The situation is far from well understood, however. Analyses of the well-water samples obtained in September 1977 showed elevated concentrations of Na, Mg, Ca, As, Al, SO_4, Cl, and Si in the well closest to the dike. However, Mg concentrations in the ash basin were lower than in any water system in the area. This phenomenon is most likely caused by leaching from the soil itself. Data in Table 15 also suggest that gradients exist for SO_4, Ca, Mg, and Na concentrations in four progressively distant well-water samples obtained north of the ash basin. However, K concentrations displayed a reverse gradient, and the highest boron concentration was found in the well farthest from the ash basin. The data from this project indicate that groundwater concentrations are neither spatially nor temporally consistent with ash basin concentrations.

Future modeling of this system will require more detailed information regarding sub-surface water movements around the ash basin in addition to better soil characterization. Any sampling must also be done in conjunction with detailed records of plant operations since interruptions in ash basin flows strongly influences infiltration into the soil column.

TABLE 15. CHEMICAL CONCENTRATIONS OF SELECTED DISSOLVED COMPONENTS IN GROUNDWATER SAMPLES FROM THE ASHPIT DIKE AND THE SEDGE MEADOW

	SO_4 (ppm)	As (ppm)	B (ppm)	Ca (ppm)	Cr (ppm)	K (ppm)	Mg (ppm)	Na (ppm)
Top well	36	<0.001	0.3	77.0	<0.005	1.6	49	6.2
Middle well	10	<0.001	0.3	60.5	<0.005	2.6	37	5.0
Bottom well	20	<0.001	0.3	42.5	<0.005	3.4	22	1.0
Sedge meadow	18	<0.001	0.7	9.6	<0.005	3.6	11	1.9

SECTION 7

ENVIRONMENTAL IMPACT ON NATURAL WATER SYSTEMS

In considering sources, mechanisms of transport, and sinks of materials in the environment, simple input/output mass balance models are often useful. Such simple models can offer initial insights into the general behavior of an element and often establish a framework for subsequent research. In the case of the cooling pond, we felt that the most useful information from such an exercise would be data on the amount of material that accumulates. It must be kept in mind that several blowdowns occurred during the sampling period. The overall effect from such efforts on mass balance calculations would tend to decrease the residence times of elements in the cooling pond, especially for the dissolved components. The interpretation of the calculated fluxes should thus be made with some caution.

Fly ash particles serve as the foremost mode of transport for trace elements entering the environment as a result of coal combustion. Moreover, trace metals are preferentially concentrated on the smallest fly ash particles (Natusch and Wallace 1974; Natusch et al. 1974). This concentration is of obvious concern for those respirable size particles released to the atmosphere, but the effects and transport of micron-size particles in an aquatic system are not as well documented. These small ash particles probably constitute a major portion of the suspended particulate matter in ash ponds. The following section presents a mass balance for selected elements in the cooling basin and a general discussion of the effects of fly ash discharge on receiving waters.

CHEMICAL MASS BALANCES OF THE COOLING POND AND ASH BASIN

Table 16 presents a mass balance for several elements in the cooling pond (including suspended particulate matter). Calculations were based on averaged data from neutron activation analysis of suspended sediments (Table 17), plant pumping records (Table 1), and values obtained from dissolved element analysis (see data acquisition report). It was assumed that leaching of solid phase elements into the groundwater represents an insignificant loss to the system except for K, Na, SO_4, and Cl. Phase partitioning of As, Ca, and Sb also indicate that these elements are amenable to groundwater transport. Because $CaCO_3$ precipitation is such a strong function of Ca concentration and temperature (see previous discussion), it is very difficult to predict how much of this will be transported away via groundwater.

TABLE 16. MASS BALANCE FOR SELECTED ELEMENTS IN THE COOLING POND

Element	Input (kg/yr)	Amount in pond (kg)	Output (kg/yr)	Groundwater outflow(kg/yr)	Percentage remaining in pond
Al	22,600 (5)[a]	2,380	4,760		79
As	104 (95)	22	44		58
Ba	800 (66)	125	232		71
Ca	565,000 (99)	136,000	271,000		52
Co	10 (20)	2	4		60
Cu	34 (8)	36	73		--
Fe	13,600 (23)	1,800	3,600		74
K	40,800 (93)	8,570	17,100	14,600	22
Na	220,750 (99)	46,360	92,700	84,700	20
Sb	6 (94)	1	3		50
Si	80,000 (32)	10,100	23,500		71
Zn	320 (25)	34	67		79
SO_4	300,000 (99)	63,000	126,000	115,000	16
PO_4	16,000 (14)	290	580		96
Cl	280,000 (99)	58,800	117,000	110,000	19
Particulate matter	270,000	56,700	84,700		70

[a]Numbers in parentheses represent the average percentage "dissolved" concentration, (that is, <0.4 m).

The model indicates that the cooling pond acts as a repository for the major fraction of elements associated with solid phases. Except for the nonreactive elements (Na, K, SO_4, and Cl), the cooling pond retains 70%, or more, of Al, Ba, Fe, Si, Zn, and PO_4. The calculations also suggest that a significant amount of Cu is added to the system from plant activities (39 kg/yr). This addition is presumed to result from the in-plant cooling system. Inspection of Table 14 indicates that some elemental enrichment of particulate matter occurs between the cooling pond intake and plant outflow. That is, particulate matter at the plant outflow exhibits higher concentrations of many insoluble elements. We speculate that chlorination and heating partially destroys the organic matrix of the particulate material.

The mass balance calculations derived from cooling pond input and output elemental concentrations indicate that: (1) Copper is released from the plant in signficant quantities; (2) most cations (except Na and K) are effectively retained by solid phase association; (3) suspended particulate matter and bottom sediments are efficient in maintaining relatively low soluble metal concentrations; and (4) the majority of P is accumulating in the sediments but could be available during anoxic conditions.

TABLE 17. NEUTRON ACTIVATION RESULTS FOR SUSPENDED SEDIMENTS COLLECTED IN THE WISCONSIN RIVER AND COOLING POND (SEPTEMBER 1976)[a]

Element	Wisconsin River stations			Cooling pond stations	
	107	108	109	105	106
As	22±3	24±3	30±3	18±2	16±3
Ba	380±50	1,330±80	500±50	560±20	760±30
Ca	34,000±7,000	19,000±6,000	17,000±5,000	17,000±3,000	
Ce	66±1	61±2	63±1	18.1±0.7	
Co	11.6±0.4	13.0±0.5	13.3±0.4	5.9±0.2	6.9±0.3
Cs	2.1±0.3	2.0±0.4	2.0±0.3	0.86±0.14	
Eu	0.81±0.02	1.09±0.04	1.00±0.03	0.306±0.01	
Fe	47,800±500	54,200±700	52,800±500	20,200±200	24,400±300
Hf	2.6±0.1	2.6±0.2	2.9±0.2	0.99±0.05	1.04±0.12
K	11,000±900	12,300±800	13,400±1,000	7,700±500	10,700±1,100
La	32.6±0.4	30.4±0.6	30.5±0.5	10.6±0.3	11.7±0.6
Lu	0.306±0.014	0.30±0.02	0.291±0.014	0.085±0.010	0.126±0.013
Na	3,210±40	3,730±70	5,400±100	2,720±30	1,730±50
Nd	43±10		35±9		25±7
Rb	37±6	46±8	44±6	20±4	26±5
Sb	3.1±0.2	2.9±0.3	3.5±0.6	1.2±0.1	1.5±0.2
Sc	7.8±0.2	8.65±0.09	8.44±0.08	2.37±0.03	3.04±0.03
Se	1.9±0.7				
Sm	6.04±0.06	5.2±0.2	5.30±0.05	1.55±0.03	2.12±0.04
Tb	0.84±0.05	0.60±0.05	0.59±0.04	0.22±0.03	0.29±0.03
Th	4.71±0.14	7.3±0.2	7.7±0.2	3.36±0.14	4.71±0.14
Yb	2.01±0.13	1.7±0.2	2.07±0.12	4.4±0.6	0.70±0.07
Zn	340±10	322±9	509±13	188±6	422±11
Suspended sediment (mg/liter)	13.9	13.1	13.6	12.3	10.6

[a] µg/g.

Table 18 presents a mass balance for several elements in the ash basin. Calculations were based on averaged data from neutron activation analysis of suspended sediments (collected at the ash basin intake and discharge), plant pumping records (Table 1), and data from the monitoring effort. Groundwater fluxes could not be calculated due to lack of accurate flow data. Similarly, no provisions have been made regarding the intermittent fly ash discharge. The data should, nevertheless, reflect typical input/output levels at the ash basin before Columbia Unit II was operational.

TABLE 18. MASS BALANCE FOR THE ASH BASIN

Element	Input (kg/yr)			Output (kg/yr)	Percent retained in ash basin
	Cooling pond	Fly ash	Total		
Al	2,380 (4)[a]	8,100,000	8,102,380	59,170 (99)	>99
As	22 (69)	2,563	2,585	315 (99)	88
Ba	125 (22)	1,040,040	1,040,165	1,015 (97)	>99
Ca	136,000 (99)	16,724,850	16,860,850	98,541 (99)	>99
Co	2 (57)	1,281	1,283	-- --	--
Cu	36 (99)	10,240	10,276	49 (99)	>99
Fe	1,800 (28)	3,891,410	3,893,210	95 (62)	>99
K	8,570 (95)	520,000	528,570	9,107 (99)	98
Na[b]	46,360 (98)	323,000	369,360	1,400,000 (99)	--
Sb	1 (97)	1,158	1,159	-- --	--
SO_4	63,000 (99)	1,152,980	1,215,980	492,520 (99)	59
Si	10,100 (12)	27,018,700	27,028,800	10,450 (94)	>99
Zn	34 (44)	9,005	9,039	12 (87)	>99

[a]Numbers in parenthesis represent average percentage "dissolved" concentrations (that is, <0.4 m).
[b]Na_2CO_3 is used in electrostatic precipitators.

The mass balance calculations around the ash basin indicate that: (1) Most of the elements reach the ash basin in particulate form and remain there; those discharged in significant quantities are in a soluble form. This is due to efficient settling of fly ash and precipitates and because high pH values solubilize certain elements; (2) with the exception of SO_4 and As (and possibly Cr, B, Se, and V), at least 99% of the measured elements are retained within the ash basin; (3) a significant quantity of Na is added to the system and passes through. The additional Na comes from Na_2CO_3 which is used to improve electrostatic precipitator efficiency; and (4) although the addition of H_2SO_4 to the ash basin effluent is effective in lowering the pH, it results in flocculation and settling of Al in the

discharge creek. Concurrent removal of other elements is also possible (by adsorption and coprecipitation).

The elemental discharge data from the ash basin has also been combined with concentration and flow data from the Wisconsin River in an effort to discern whether their releases influence the water quality of the river. It must again be kept in mind that these calculations are based on yearly averaged data, that some elements will deposit in Rocky Run Creek (for example, Al and Ba), and that no distinction has been made for soluble and particulate phases. The results from these calculations should, however, be representative to within a factor of two or three and are presented in Table 19.

TABLE 19. POSSIBLE ELEMENTAL CONCENTRATION CHANGES IN WISCONSIN RIVER DUE TO ASH BASIN DISCHARGE[a]

Element	% concentration change
Al	0.97
As	1.1
B	3-5
Ba	0.5
Ca	0.6
Cr	1-4
Cu	0.5
Fe	0.003
K	0.08
Na	2.5
Si	0.05
So_4	0.6
Zn	0.01

[a]Calculations based on an annual Wisconsin River flow of 5.3×10^{12} liters/year (Andrews and Anderson 1976).

These calculations indicate that the elemental discharge from the ash basin has a negligible effect on the water quality of the Wisconsin River. Although Na, B, and Cr may represent possible exceptions, it would not be feasible to measure concentration changes on site, because the accuracy and precision of analytical procedures are usually between 5 and 10%. Similar conclusions would hold for other elements not presented in Table 18 (such as Pb, Cd, V, Se, Sb, and U). Although several elements are elevated in the ash basin effluent, the dilution ratio between the discharge creek and Wisconsin River is about 1:270. Any significant biological effect, resulting from ash basin discharge of chemicals, should thus confined to Rocky Run Creek.

THE EFFECT OF FLY ASH DISCHARGE AND STORAGE ON RECEIVING WATERS

This study has shown that the largest fraction of the trace elements entrained in this system reside in the particulate form. However, when these particles are discharged from a primarily inorganic system to receiving waters of different origin, the trace element distribution may be altered. A pH decrease might cause some fraction of the trace elements (cations) to be released to the dissolved phase despite their strong electrostatic attraction to the ash surface. In addition, the organic matter present in receiving waters will tend to solubilize trace metals such as such as Cd, Cu, Pb, and Zn by chelation and complexation reactions. The extent of these organo-metallic interactions clearly depends upon the composition of the receiving water. Natural waters, such as the Wisconsin River, that contain large amounts of humic and fulvic acids should experience these types of organo-metallic interactions.

Acidic rainfall on ash disposal sites could also mobilize trace elements. Extensive data is not available describing rainwater leaching of trace elements from fly ash. In a preliminary series of experiments, conducted to estimate this leaching potential, Natusch (1975) observed that 5 to 30% of the toxic elements (for example, Cd, Cu, and Pb) are leachable. This equilibrium leaching study indicates that at least 10% (as per p. 91) of the cadmium would be solubilized based on acid rain pH values of 3.0 to 5.0 reported for the northern United States by Galloway et al. (1976), Beamish and Van Loon (1977), and Murphy (1974). Of course, if this leaching occurred in the ash pond it would be suppressed by solution equilibria as described previously. However, in other ash landfill areas the metallic burden of leachate waters may be directly exposed to the surrounding environment. Benninger et al. (1975), using ^{210}Pb as a heavy metal tracer, demonstrated the strong sequestering of dissolved trace metals by organic rich soils. Less than 2% of the ^{210}Pb supplied to the terrain was transmitted to groundwaters. Similar results of efficient trace metal scavenging by suspended particulate matter in the Colorado River was observed earlier by Rama and Goldberg (1961). Using these data, Benninger et al. (1975) calculated that only 0.02%/yr of the metals residing in the Susquehanna River watershed are transported out of the system under normal weathering and erosion conditions. This calculation implies that adsorption processes and soil organo-metallic interactions should scavenge a large fraction of the trace elements in fly ash leachate waters.

Some evidence indicates that groundwater can be contaminated by ash basin water. Well samples adjacent to the Columbia ash basin may sporadically exhibit higher dissolved concentrations of arsenic, boron and sulfate than groundwaters farther away from the dike. Obviously, there is a finite quantity which may be retained by soil underlying and surrounding an ash disposal site. When this potential is exceeded, contamination of groundwater and close-by streams, rivers, or lakes is possible.

Fly ash particles, on the other hand, may act as a sink for trace elements under certain environmental conditions. Adsorption of trace cations may occur when the pH is above 7.55. These pH conditions are typical for natural water systems (Stumm and Morgan 1970). The hydrous oxide surface coating of aluminum and iron encompassing the ash particles provide an excellent substrate for adsorption of trace metals. Such surfaces have a large adsorption capacity for many species (Fox 1968, Shukla et al. 1971). These interactions may be significant in the surface organic microlayer (SOM) of freshwater lakes where the atmospheric input of particulates, including fly ash, is important. After deposition, subsequent trace element enrichment of these anthropogenic particulates will undoubtedly occur. These particles may then return to the atmosphere by bubble injection (MacIntyre 1974, Wallace and Duce 1975) or interact with biological and chemical components of the lake (Elzerman 1976).

Other elements like calcium, potassium, magnesium, and sodium will be readily released to the dissolved phase as fly ash particles enter natural waters either by natural weathering processes or atmospheric deposition. These elements are of no apparent toxicological concern, but a pH rise may occur in natural waters having an insufficient buffering capacity to neutralize their hydrolytic dissolution reactions. Any pH increase due to these reactions should be a localized effect. The magnitude of such a pH change is explicitly a function of the fly ash/water ratio and the buffering capacity of the particular receiving water.

A more important effect with regard to the overall water quality may be the lowering of the phosphorus content by co-precipitation with calcium and/or magnesium phases. This precipitation phenomena would decrease the fertility of a water body. Furthermore, this process may be enhanced in calcareus lakes commonly encountered in the north central U.S. Previous studies performed by Tenney and Echelberger (1970) and Higgins et al. (1976) indicate the vehicle for inorganic phosphorus removal from lake waters after fly ash addition is precipitation of amorphous calcium-phosphates. Both of these studies, however, employed large solid to solution ratios (e.g. 10 g/liter). Dilution of ash pond waters by receiving waters may effectively decrease solid-solution ratios of ash pond discharges so this phenomena becomes unimportant during normal flow periods. In fact, only a few mg/liter suspended solid load exists downstream of the ash pond drain at the Columbia site (Andren et al. 1976).

The input of phosphorus and silica to a water body by fly ash dissolution could be important in terms of influencing the biological make-up of that system. Fly ash particles may contribute large amounts of silica and perhaps in some cases significant quantities of phosphorus. At pH values of natural water systems (7.0 to 9.0) phosphorus should be released from the ash particle to the dissolved phase. Since the phosphorus content of the Columbia fly ash is less than 1%, it is probably too small a quantity to be of importance for most freshwater lakes. It is very likely that the particles containing the phosphorus may sink to the sediments of rivers or shallow lakes before much of the phosphorus dissolves. It also appears that prior dissolution of surface constituents, i.e., sulfate coating, is necessary before phosphorus becomes directly available to the bulk

solution. Several days in an aquatic environment may be required for this coating to dissolve (Talbot 1977, Helmke et al. 1977).

Silica should dissolve from the fly ash over a wide pH range, as was demonstrated by its pH dependence. Diatoms may utilize this silica as it dissolves. The remaining silica will probably be deposited in the sediments, where it may then be incorporated into the silica cycle of the lake (Vigon 1976). Although silica comprises about 23% of the Columbia fly ash, introduction of a large quantity of fly ash would most likely be needed before this became a major silica supply for diatoms. Lastly, a desirable lake management goal of establishing a viable diatom population to control objectional algae blooms in eutrophic lake waters might include lake treatment with fly ash. Further research is needed, however, to ensure that toxic trace elements, (including transistion metals and anions like arsenic or boron) are adequately removed by pretreatment or are in low enough concentrations to constitute its use in such lake restoration projects.

REFERENCES

American Public Health Association, American Water Works Association, and Water Pollution Control Federation. 1971. Standard methods for the examination of water and waste water. 13th Ed.

American Public Health Association, American Water Works Association, and Water Pollution Control Federation. 1974. Standard methods for the examination of water and waste water. 14th Ed.

Anderson, M. P., and C. B. Andrews. 1976. Hydrogeology. In: Documentation of environmental change related to the Columbia Electric Generating Station. Report 66. Institute for Environmental Studies, Univ. of Wisconsin, Madison.

Anderson, W. L., and K. E. Smith. 1977. Dynamics of mercury at a coal-fired power plant and adjacent cooling lake. Environ. Sci. Technol. 11:75-80.

Andren, A. W., M. A. Anderson, N. Loux, and R. W. Talbot. 1976 . Aquatic chemistry. In: Documentation of environmental change related to the Columbia Electric Generating Station. Report 69. Institute for Environmental Studies, Univ. of Wisconsin, Madison.

Andren, A. W., M. A. Anderson, N. Loux, and R. W. Talbot. 1977. Aquatic chemistry. p. 143-170. In: Documentation of environmental change related to the Columbia Electric Generating Station. Report 82. Institute for Environmental Studies, Univ. of Wisconsin, Madison.

Beamish, R. J., and J. C. Van Loon. 1977. Precipitation loading of acid and heavy metals to a small acid lake near Sudbury, Ontario. J. Fish. Res. Board Can. 34:649-658.

Benninger, L. K., D. M. Lewis, and K. K. Turekian. 1975. The use of natural Pb-210 as a heavy metal tracer in the river-estuarine system. p. 202-210. In: Thomas M. Church (ed.) Marine chemistry in the coastal environment, Am. Chem. Soc., Washington, D.C..

Berner, R. A. 1975. The role of magnesium in the crystal growth of calcite and aragonite from sea water. Geochim. Cosmochim. Acta. 39:489-504.

Braunstein, H. M., E. D. Copenhaver, and H. A. Pfuderer (eds.). 1977. Environmental, health, and control aspects of coal conversion: An information overview. ORNL/EIS-95. Vols. I and II. Oak Ridge National Laboratory, Oak Ridge, Tenn.

Bricker, O. P., and R. M. Garrels. 1967. Mineralogic factors in natural water equilibria. p. 449-469. In: S.D. Faust and J.V. Hunter (eds.) Principles and applications of water chemistry, John Wiley, New York.

Brimblecombe, P., and D. J. Spedding. 1975. The dissolution of iron from ferric oxide and pulverized fuel ash. Atmos. Environ. 9:835-838.

Brink, R. H., and W. J. Halstead. 1956. Studies relating to the testing of fly ash for use in concrete. In: Am. Soc. Testing Material. 56:1161-1214.

Brumbay, R.U. 1972. Qualitative analysis. Harper and Row, New York.

Chamberlain, D. G., and R. E. Anderson. 1971. Selective removal of zinc from tower blowdown by ion exchange. Indus. Water Eng. 8:33.

Cherry, D. S., and R. K. Guthrie. 1977. Toxic metals in surface waters from coal ash. Water Res. Bull. 13:1227-1236.

Cherry, D. S., R. K. Guthrie, J. H. Rogers, J. Cairns, and K. L. Dickson. 1976. Responses of mosquitofish (*Gambusia affinis*) to ash effluent and thermal stress. Trans. Am. Fish. Soc. 105:686-694.

Corsaro, G., and S. Sutherland. 1967. The formationn and behavior of hydroxyapatite. p. 470-490. In: S.D. Faust and J.V. Hunter (eds.) Principles and applications of water chemistry, John Wiley, New York.

Cotton, F. A., and G. Wilkinson. 1972. Advanced inorganic chemistry. Interscience Publishers, New York.

Coutant, C. C., C. S. Wasserman, M. S. Chung, D. B. Rubin, and M. Manning. 1978. Chemistry and biological hazard of a coal ash seepage stream. J. Water Pollut. Control Fed. 50:747-753.

Davison, R. L., D. F. S. Natusch, J. R. Wallace, and C. A. Evans, Jr. 1974. Trace elements in fly ash: Dependence of concentration on particle size. Environ. Sci. Technol. 8:1107-1113.

Eggett, J. M., and T. M. Thorpe. 1973. Mobilization of chromium from fly ash particulates by aqueous systems modeling natural waters. J. Environ. Sci. Health 4:295-313.

Eisenrich, S. J., R. T. Bannerman, and D. E. Armstrong. 1975. A simplified phosphorus analysis technique. Environ. Lett. 9:43-53.

Elzerman, A. W. 1976. Surface microlayer-microcontaminant interactions in freshwater lakes. Ph.D. Dissertation, Univ. of Wisconsin, Madison.

Fox, R. L. 1968. National Research Council, Washington, D.C. In: M. Drosdoff (ed) Soils of the humid tropics.

Galloway, J. N., G. E. Likens, and E. S. Edgerton. 1976. Acid precipitation in the northeastern United States: pH and acidity. Science 194:722-724.

Garrels, R. M., and C. L. Christ. 1965. Solutions, minerals, and equilibria. Freeman, Cooper and Co., San Francisco, Calif.

Garrels, R. M., and F. T. Mackenzie. 1967. Origin of the chemical composition of some springs and lakes. p. 222-242. In: R.F. Gould (ed.) Equilibrium concepts in natural water systems, Am. Chem. Soc., Washington, D.C.

Gibbs, R. J. 1965. Error due to segregation in quantitative clay mineral X-ray diffraction mounting techniques. Am. Mineral. 50:741-751.

Helmke, P. A., W. Robarge, M. Schoenfield, and J. Thresher. 1977. Trace elements. p.232-238. In: Documentation of environmental change related to the Columbia Electric Generating Station. Report 82. Institute for Environmental Studies, Univ. of Wisconsin, Madison.

Hem, J. D. 1971. Study and interpretation of the chemical characteristics of natural water. Water-Supply Paper 1473, U.S. Geological Survey. Washington D.C.

Hem, J. D., C. E. Robertson, C. J. Lind, and W. L. Polzer. 1973. Chemical interactions of aluminum with aqueous silica at 25°C. Water-Supply Paper 1827-E, U.S. Geological Survey, Washington, D.C.

Higgins, B. P., S. C. Mohleji, and R. L. Irvine. 1976. Lake treatment with fly ash, lime, and gypsum. J. Water Pollut. Control Fed. 48:2153-2164.

Holland, W., K. Wilde, J. Parr, P. Lowell, and R. Pohler. 1975. Environmental effects of trace elements from ponded ash and scrubber sludge. Radian Corp., Report No. PB252090. 265 pp.

Holliday, R., D. R. Hodgson, W. N. Townsend, and J. W. Wood. 1958. Plant growth on fly ash. Nature 181:1079-1080.

Huang, C. P. 1975. Adsorption of phosphate at the hydrous Al_2O_3-electrolyte interface. J. Colloid Sci. 53:178-186.

Jenkins, D., J. F. Ferguson, and A. B. Menar. 1971. Chemical processes for phosphate removal. Water Res. 5:369-389.

John, E. D., and G. J. Nickless. 1977. Chromatography 138:399-412.

Jones, L. H., and A. V. Lewis. 1960. Weathering of fly ash. Nature 185:404-405.

Klein, D. H., A. W. Andren, and N. E. Bolton. 1975. Trace element discharges from coal combustion for power production. Water Air Soil Pollut. 5:71-77.

Korte, N. E., J. Skopp, E. E. Niebla, and W. H. Fuller. 1975. A baseline study on trace metal elution from diverse soil types. Water Air Soil Pollut. 5:149-156.

Langmuir, D. 1968. Stability of calcite based on aqueous solubility measurements. Geochim. Cosmochim. Acta. 32:835-851.

Langmyhr, F. J., and P. E. Paus. 1968. The analysis of inorganic siliceous materials by atomic adsorption spectrophotometry and the hydrofluoric acid decomposition technique. Anal. Chim. Acta. 43:397-408.

Linton, R. W., A. Loh, D. F. S. Natusch, C. A. Evans, Jr., and P. Williams. 1976. Surface predominance of trace elements in airborne particles. Science 191:852-854.

MacIntyre, F. 1970. Geochemical fractionation during mass transfer from sea to air by breaking bubbles. Tellus 22:451-462.

MacIntyre, F. 1974. Chemical fractionation and sea-surface microlayer processes. p. 245-299. In: E.D. Goldberg (ed.) The sea. Vol. 5 Marine chemistry. Wiley-Interscience, New York.

Malotky, D. T. 1978. The adsorption of hydrolyzable ions on hydrous metal oxides. Ph.D. Disseration. Univ. of Wisconsin, Madison.

Murphy, J., and J. P. Kiley. 1962. A modified single solution method for the determination of phosphate in natural waters. Anal. Chim. Acta. 27:31-36.

Murphy, T. J. 1974. Sources of phosphorus inputs from the atmosphere and their significance to oligotrophic lakes. Research Report 92. Water Resources Center, Univ. of Illinois, Champaign-Urbana. 45 p.

Natusch, D. F. S. 1975. Characteristics of pollutants from coal combustion and conversion processes. p. 73-90. In: Toxic effects on the aquatic biota from coal and oil shale development. (Quarterly progress report: October-December) Natural Resources Ecology Laboratory, Colorado State University, Fort Collins.

Natusch, D. F. S. 1976. Characteristics of pollutants from coal combustion and coal/oil shale conversion processes. p. 85-98. In: Toxic effects on the aquatic biota from coal and oil shale development (Quarterly progress report: January-March) Natural Resources Ecology Laboratory, Colorado State University, Fort Collins.

Natusch, D. F. S., and J. R. Wallace. 1974. Urban aerosol toxicity: The influence of particle size. Science 186:695-699.

Natusch, D. F. S., J. R. Wallace, and C. A. Evans, Jr. 1974. Toxic trace elements: Preferential concentration in respirable particles. Science 183:202-204.

Novozamsky, I., J. Beck, and G. H. Bolt. 1976. Chemical equilibria. p. 13-42. In: G. H. Bolt and M. G. M. Bruggeninert (eds.) Soil chemistry, Elsevier Scientific, New York.

Okura, T., K. Goto, and T. Yotuyangi. 1962. Forms of aluminum determined by an 8-quinolate extraction method. Anal. Chem. 34:581-582.

Parekh, P. P., P. Moller, and P. Dulski. 1977. Distribution of trace elements between carbonate and non-carbonate phases of limestone. Earth Planet. Sci. Lett. 34:35-50.

Parks, G. A. 1972. Free energies of formation and aqueous solubilities of aluminum hydroxides and oxide hydroxides at 25°C. Am. Minerol. 57:1163-1189.

Perkin-Elmer. 1975. Analytical methods for atomic adsorption spectroscopy using the HGA graphite furnace.

Piwoni, M. D. 1974. A limnological survey of selected impoundments in central and southern Wisconsin. M.S. Thesis, Univ. of Wisconsin, Madison.

Rama, M. K., and E. D. Goldberg. 1961. Lead-210 in natural waters. Science 134:98-99.

Rees, W. J., and G. H. Sidrak. 1956. Plant nutrition on fly ash. Plant Soil 8:141-159.

Resources Agency of California. 1960. Water quality criteria. State Water Quality Control Board.

Robie, R. A., and D. R. Waldbaum. 1968. Thermodynamic properties of minerals and related substances at 298.15°K (25.0°C) and one atmosphere (1.013 bars) pressure and at high temperature. Bull. No. 1259. U.S. Geological Survey, Washington, D.C.

Sams, B. L., J. K. G. Silvey, and J. A. Stanford. 1978. Comparative chemistry of a cooling reservoir and its water source. J. Water Pollut. Control Fed. 50:193-201.

Schindler, P. 1967. Heterogeneous equilibria involving oxides, hydroxides, carbonates, and hydroxide carbonates. In: R. F. Gould (ed.) Equilibrium concepts in natural water systems, Am. Chem. Soc., Washington, D.C.

Shannon, D. G., and L. O. Fine. 1974. Cation solubilities of lignite fly ashes. Environ. Sci. Technol. 8:1026-1028.

Shukla, S. S., J. K. Syers, J. D. H. Williams, D. E. Armstrong, and R. F. Harris. 1971. Sorption of inorganic phosphate by lake sediments. Soil Sci. Soc. Am. Proc. 35:244-249.

Sigma Research, Inc. 1975. Report of a workshop on the impact of thermal power plant cooling systems on aquatic environment. Special Report 38, Vols. I and II. 28 September-2 October 1975.

Sonzogni, W.C. 1972. Effect of nutrient input reduction on the eutrophication of the Madison lakes. Ph.D. Disseration, Univ. of Wisconsin, Madison.

Stratton, C. L., and G. F. Lee. 1975. Cooling towers and water quality. J. Water Pollut. Control Fed. 47:1901-1912.

Strickland, J. D. H., and T. R. Parsons. 1968. A practical handbook of seawater analysis. Fish. Res. Board Can., Ottawa, Canada.

Stumm, W., and J. J. Morgan. 1970. Aquatic chemistry: An introduction emphasizing chemical equilibria in natural waters. Wiley-Interscience, New York.

Syers, J. K., R. F. Harris, and D. E. Armstrong. 1973. Phosphate chemistry in lake sediments. J. Environ. Qual. 2:1-14.

Talbot, R. W. 1977. Heterogeneous equilibria in a fly ash pond. M.S. Thesis, Univ. of Wisconsin, Madison.

Talbot, R. W., M. A. Anderson, and A. W. Andren. 1978. Qualitative model of heterogeneous equilibria in a fly ash pond. Environ. Sci. Technol. 12:1056-1062.

Tenney, M. W., and W. F. Schelberger, Jr. 1970. Fly ash utilization in the treatment of polluted waters. U.S. Bumines Circ. No. 8488, Washington, D.C. p. 237-268.

Theis, T. L., and R. O. Richter. 1978. Chemical speciation of heavy metals in power plant ash pond leachate. 33rd Purdue Industrial Waste Conf.

Theis, T. L. and J. L. Wirth. 1977. The sorbtive behavior of trace metals on fly ash in aqueous systems. Environ. Sci. Technol. 11:1096.

Van Hook, R. I., and W. D. Shutts. 1976. Effects of trace contaminants from coal combustion. Proc. of workshop, ERDA 77-64. Knoxville, Tenn.

Vigon, B. W. 1976. The role of silica and the vernal diatom bloom in controlling the growth of nuisance algal populations in lakes. M.S. Thesis. Univ. of Wisconsin-Madison, Madison, Wis.

Vollenweider, R. A. 1968. The scientific basis of lake and stream eutrophication with particular reference to phosphorous and nitrogen as eutrophication factors. Technical Report DAS CSI 68/27, DECD, Paris, France.

Wachter, R. A., and T. R. Blackwood. 1978. Source assessment: Water pollutants from coal storage areas. U.S. Environmental Protection Agency, EPA 600/2-78-004, Washington, D.C.

Wallace, G. T., and R. A. Duce. 1975. Concentration of particulate trace metals and particulate organic carbon in marine surface waters by bubble flotation mechanism. Mar. Chem. 3:157-181.

Welch, K. J. 1979. Coal related polycyclic aromatic hydrocarbons and their aqueous chlorination chemistry. M.S. Thesis, Univ. of Minnesota, Duluth.

Westall, J. C., J. L. Zachary, and F. M. M. Morel. 1976. MINEQL: A complete program for the calculation of chemical equilibrium composition of aqueous systems. Report No. T 76-6. Dep. of Civil Engineering, Massachusetts Inst. of Technology, Cambridge, Mass.